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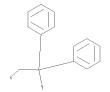
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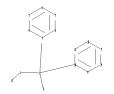
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chain nodes :
1  2  16  17
ring nodes :
3  4  5  6  7  8  9  10  11  12  13  14
chain bonds :
1-2  1-17  2-3  2-10  2-16
ring bonds :
3-4  3-8  4-5  5-6  6-7  7-8  9-10  9-14  10-11  11-12  12-13  13-14
exact/norm bonds :
2-16
exact bonds :
1-2  1-17  2-3  2-10
normalized bonds :
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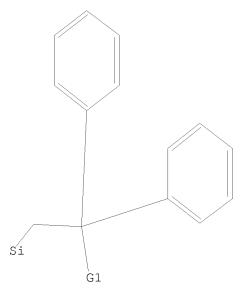
G1:CH3,H

Match level:
1:CLASS 2:CLASS 3:Atom 4:Atom 5:Atom 6:Atom 7:Atom 8:Atom 9:Atom 10:Atom 11:Atom 12:Atom 13:Atom 14:Atom 16:CLASS 17:CLASS

L1 STRUCTURE UPLOADED

=> d 11

L1 HAS NO ANSWERS



G1 Me,H

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=> s 11 sss full FULL SEARCH INITIATED 15:07:34 FILE 'REGISTRY' FULL SCREEN SEARCH COMPLETED - 6827 TO ITERATE

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L2 44 SEA SSS FUL L1

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=> s 12

L3 30 L2

=> d 13 1-30 abs ibib hitstr

L3 ANSWER 1 OF 30 CAPLUS COPYRIGHT 2008 ACS on STN

The Yb(II) hydride complex (DIPP-nacnac) YbH·THF (3-Yb, DIPP-nacnac) = CH{(CMe)(2,6-iPr2C6H3N)}2) was prepared by a mild metathesis reaction of (DIPP-nacnac) Yb[N(SiMe3)2]·THF with PhSiH3. 3-Yb crystallizes as a dimer with bridging hydride ions, and its geometry is similar to that of the analog Ca hydride complex (3-Ca). 3-Yb is well soluble in benzene and remarkably stable in solution at room temperature Ligand exchange to the homoleptic Yb(II) complexes takes place at higher temps. (3-Yb is less stable than the analog 3-Ca). The soluble hydride complexes 3-Ca and 3-Yb are catalysts for the hydrosilylation of 1,1-diphenylethylene, but differences in the product distributions are observed Slow hydrolysis of (DIPP-nacnac)Yb[N(SiMe3)2]·THF gave reduction of H2O and unidentified Yb(III) complexes. Fast hydrolysis at low temperature, however, resulted in

the

1st Yb(II) hydroxide complex, (DIPP-nacnac)Yb(OH)·THF (4-Yb, 20% yield), which is a dimer with bridging hydroxide ions in the solid state. The crystal structure is isomorphous to that of the Ca analog 4-Ca. 4-Yb is well soluble in benzene and considerably more stable against ligand exchange and formation of homoleptic species than 3-Yb.

ACCESSION NUMBER: 2007:581030 CAPLUS

DOCUMENT NUMBER: 147:225397

TITLE: Syntheses and Structures of Ytterbium(II) Hydride and Hydroxide Complexes: Similarities and Differences with

Their Calcium Analogues

AUTHOR(S): Ruspic, Christian; Spielmann, Jan; Harder, Sjoerd CORPORATE SOURCE: Anorganische Chemie, Universitaet Duisburg-Essen,

Essen, 45117, Germany

SOURCE: Inorganic Chemistry (Washington, DC, United States)

(2007), 46(13), 5320-5326 CODEN: INOCAJ; ISSN: 0020-1669

PUBLISHER: American Chemical Society

DOCUMENT TYPE: Journal LANGUAGE: English

OTHER SOURCE(S): CASREACT 147:225397

IT 896100-18-8P

RL: SPN (Synthetic preparation); PREP (Preparation)

(preparation from hydrosilylation of diphenylethylene catalyzed by ytterbium(II) and calcium bis(diisopropylphenyl)pentanediiminato hydrido complexes)

RN 896100-18-8 CAPLUS

CN Benzene, 1,1'-[2-(phenylsily1)ethylidene]bis- (CA INDEX NAME)

REFERENCE COUNT: 47 THERE ARE 47 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L3 ANSWER 2 OF 30 CAPLUS COPYRIGHT 2008 ACS on STN GI

AB A regio-/chemoselective silylmetalation of various functionalized alkenes, e.g. I, based on the zinc silyl complex in the presence of a catalytic amount of copper cyanide was developed. Silylmetalation of alkenes, followed by electrophilic trapping, proved to be a powerful tool for the functionalization of the continuous carbon atoms of the alkenes. The resultant alkylsilanes, e.g. II, can be converted smoothly into alcs., e.g. III, by oxidative cleavage of the carbon-silicon bond.

ACCESSION NUMBER: 2006:1324372 CAPLUS

DOCUMENT NUMBER: 146:228990

TITLE: Regio- and Chemoselective Silylmetalation of

Functionalized Terminal Alkenes

AUTHOR(S): Nakamura, Shinji; Uchiyama, Masanobu

CORPORATE SOURCE: Graduate School of Pharmaceutical Sciences, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo,

113-0033, Japan

SOURCE: Journal of the American Chemical Society (2007),

129(1), 28-29

CODEN: JACSAT; ISSN: 0002-7863

PUBLISHER: American Chemical Society

DOCUMENT TYPE: Journal LANGUAGE: English

OTHER SOURCE(S): CASREACT 146:228990

IT 925207-60-9P

RL: SPN (Synthetic preparation); PREP (Preparation) (preparation of  $\alpha$ -substituted alkylsilanes via regio- and chemoselective copper-catalyzed silylzincation and electrophilic substitution from terminal alkenes, and preparation of  $\alpha$ -substituted alcs. via Fleming-Tamao oxidation of alkylsilanes)

RN 925207-60-9 CAPLUS

CN Benzene, 1,1'-[2-(dimethylphenylsilyl)ethylidene]bis- (CA INDEX NAME)

$$\begin{array}{c} \text{Ph} \\ | \\ \text{Me-Si-CH}_2\text{-CHPh}_2 \\ | \\ \text{Me} \end{array}$$

39 THERE ARE 39 CITED REFERENCES AVAILABLE FOR THIS REFERENCE COUNT: RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L3 ANSWER 3 OF 30 CAPLUS COPYRIGHT 2008 ACS on STN

AΒ Clean conversion of conjugated alkenes with exclusive formation of one regioisomer is achieved by using a new class of hydrosilylation catalysts based on early main-group metals (Ca, Sr, and K). The regioselectivity can be switched to the other isomer through the choice of the metal and solvent polarity. E.g., solventless hydrosilylation of CH2:CPh2 with PhSiH3 in presence of 2.5% of homoleptic L2Ca(THF)2 or L2Sr(THF)2 (L = o-Me2NC6H4CHSiMe3) at 50° gave >98% conversion to PhH2SiCPh2Me, whereas the same reactions in THF gave >98% conversion to the other regioisomer, PhH2SiCH2CHPh2.

ACCESSION NUMBER: 2006:451798 CAPLUS

DOCUMENT NUMBER: 145:103764

TITLE: Hydrosilylation of alkenes with early main-group metal

catalysts

Buch, Frank; Brettar, Julie; Harder, Sjoerd AUTHOR(S): CORPORATE SOURCE:

Anorganische Chemie, Universitaet Duisburg-Essen,

Essen, 45117, Germany

SOURCE: Angewandte Chemie, International Edition (2006),

45(17), 2741-2745

CODEN: ACIEF5; ISSN: 1433-7851 Wiley-VCH Verlag GmbH & Co. KGaA

DOCUMENT TYPE: Journal LANGUAGE: English

OTHER SOURCE(S): CASREACT 145:103764

896100-18-8P

PUBLISHER:

RL: SPN (Synthetic preparation); PREP (Preparation)

(regioselectivity of hydrosilylation of conjugated alkenes with early

main-group metal catalysts)

RN 896100-18-8 CAPLUS

CN Benzene, 1,1'-[2-(phenylsily1)ethylidene]bis- (CA INDEX NAME)

Ph<sub>2</sub>CH-CH<sub>2</sub>-SiH<sub>2</sub>-Ph

REFERENCE COUNT: THERE ARE 51 CITED REFERENCES AVAILABLE FOR THIS 51 RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L3 ANSWER 4 OF 30 CAPLUS COPYRIGHT 2008 ACS on STN

AB A siloxane compound having a high refractive index comprises at least 2 silicon atoms linked by oxygen and at least one silicon-bonded substituent of the general formula -(0)x-R'-Ar2, where R' is a divalent hydrocarbon radical, x is 0 or 1, and each Ar is independently an optionally substituted aryl group, and both optionally substituted aryl groups are linked directly to the same carbon atom in the R' group, except that when only one group -(0)x-R'-Ar2 is present in the siloxane, either the siloxane contains at least 3 silicon atoms or, when the siloxane contains only 2 silicon atoms, R' equals dimethylene. The siloxanes have refractive indexes above 1.53 or even above 1.55 which is exceptional for traditional silicones. The invention also relates to siloxane-containing cosmetic compns., such as color cosmetic compns., lipsticks, nail

varnishes, mascaras, foundation creams, compact powders, hair colorants, hair dyes, and hair conditioners. Thus, 1,1-diphenylethylene (100 g, 0.55 mol) and tetramethyldisiloxane (40 g, 0.29 mol) were heated in the presence of a platinum catalyst at  $100^{\circ}$  for 2-3 h, raising the temperature to  $128^{\circ}$  over 5 h, and heating at  $128^{\circ}$  for 24 h to provide the resp. siloxane substituted with two diphenylethyl groups and having a refractive index of 1.5599.

ACCESSION NUMBER: 2005:14405 CAPLUS

DOCUMENT NUMBER: 142:114269

TITLE: Siloxane compounds having high refractive index for

cosmetic applications

INVENTOR(S): Butler, Derek William; Caprasse, Virginie Francoise

Marie Juliette; MacKinnon, Iain Alasdair; Moloney,

Grainne M.; Van Reeth, Isabelle

PATENT ASSIGNEE(S): Dow Corning Corporation, USA

SOURCE: PCT Int. Appl., 20 pp.

CODEN: PIXXD2

DOCUMENT TYPE: Patent LANGUAGE: English

FAMILY ACC. NUM. COUNT: 1

PATENT INFORMATION:

	PATENT NO.				KIND		DATE		APPLICATION NO.					DATE				
	WO 2005000856 WO 2005000856								WO 2004-EP11021				20040210					
	W:	ΑE,	AG,	AL,	AM,	ΑT,	ΑU,	ΑZ,	BA,	BB,	ВG,	BR,	BW,	BY,	BZ,	CA,	CH,	
		CN,	CO,	CR,	CU,	CZ,	DE,	DK,	DM,	DZ,	EC,	EE,	EG,	ES,	FΙ,	GB,	GD,	
		GE,	GH,	GM,	HR,	HU,	ID,	IL,	IN,	IS,	JP,	KΕ,	KG,	KP,	KR,	KΖ,	LC,	
		LK,	LR,	LS,	LT,	LU,	LV,	MA,	MD,	MG,	MK,	MN,	MW,	MX,	MZ,	NA,	NΙ,	
		NO,	NΖ,	OM,	PG,	PH,	PL,	PT,	RO,	RU,	SC,	SD,	SE,	SG,	SK,	SL,	SY,	
		ТJ,	TM,	TN,	TR,	TΤ,	TZ,	UA,	UG,	US,	UZ,	VC,	VN,	YU,	ZA,	ZM,	ZW	
	RW:	BW,	GH,	GM,	KE,	LS,	MW,	MZ,	SD,	SL,	SZ,	${\sf TZ}$ ,	UG,	ZM,	ZW,	ΑM,	ΑZ,	
			•		•		ТJ,											
							HU,											
					CF,	CG,	CI,	CM,										ΤG
PRIORITY APPLN. INFO.: GB 2003-2978 A 20030211																		
	R SOURCE						142:	1142	69									
IT	IT 820207-12-3P 820207-13-4P																	
RL: COS (Cosmetic use); IMF (Industrial manufacture); BIOL (Biological																		
study); PREP (Preparation); USES (Uses)																		
(siloxane compds. having high refractive index for cosmetic																		
applications)																		
	RN 820207-12-3 CAPLUS																	
CN Disiloxane, 1-(2,2-diphenylethyl)-1,1,3,3-tetramethyl-4-(phenylmethyl)- (CA INDEX NAME)																		

RN 820207-13-4 CAPLUS

CN Disiloxane, 1-(2,2-diphenylethyl)-1,1,3,3-tetramethyl-3-octyl- (CA INDEX NAME)

IT 820207-10-1P 820207-11-2P

RL: COS (Cosmetic use); IMF (Industrial manufacture); PRP (Properties); BIOL (Biological study); PREP (Preparation); USES (Uses)

(siloxane compds. having high refractive index for cosmetic applications)

RN 820207-10-1 CAPLUS

CN Disiloxane, 1,3-bis(2,2-diphenylethyl)-1,1,3,3-tetramethyl- (CA INDEX NAME)

RN 820207-11-2 CAPLUS

CN Disiloxane, 1-(2,2-diphenylethyl)-1,1,3,3-tetramethyl-3-(2-phenylpropyl)-(CA INDEX NAME)

IT 820207-15-6P 820207-16-7P

RL: IMF (Industrial manufacture); PRP (Properties); RCT (Reactant); PREP (Preparation); RACT (Reactant or reagent)

(siloxane compds. having high refractive index for cosmetic applications)

RN 820207-15-6 CAPLUS

CN Trisiloxane, 1,3,5-tris(2,2-diphenylethyl)-1,1,3,5,5-pentamethyl- (CA INDEX NAME)

RN 820207-16-7 CAPLUS

CN Disiloxane, (2,2-diphenylethyl)pentamethyl- (9CI) (CA INDEX NAME)

ΙT 53888-97-4P 820207-14-5P

> RL: IMF (Industrial manufacture); RCT (Reactant); PREP (Preparation); RACT (Reactant or reagent)

(siloxane compds. having high refractive index for cosmetic applications)

RN 53888-97-4 CAPLUS

CN Silane, dichloro(2,2-diphenylethyl)methyl- (9CI) (CA INDEX NAME)

$$\begin{array}{c|c} \operatorname{C1} & \\ | \\ \operatorname{Me-Si-CH}_2 - \operatorname{CHPh}_2 \\ | \\ \operatorname{C1} \end{array}$$

820207-14-5 CAPLUS

Silane, chloro(2,2-diphenylethyl)dimethyl- (9CI) (CA INDEX NAME)

ANSWER 5 OF 30 CAPLUS COPYRIGHT 2008 ACS on STN L3

(1,2-Dichloroethyl)trichlorosilane (2) reacted with a 6-fold excess of mono-, di-, and trichlorobenzenes at 120° in the presence of aluminum chloride to give regiospecific (2,2-diarylethyl)trichlorosilanes via a carbocation rearrangement. The yields were 61-69%, and regioisomers of (1,2-diarylethyl)silanes were not obtained. Alkylation of 1,2,3,4-tetrachlorobenzene with 2 did not give [2,2bis(tetrachlorophenyl)ethyl]trichlorosilane or 9,10-bis(silyl)methyl-9,10dihydroanthracenes but gave cyclic silyl-substituted indanes in 84% yield via the acid-catalyzed dimerization of  $\beta$ -(trichlorosily1)styrene formed by the first alkylation, followed by dehydrochlorination. structure of 1,2-trans-2,3-trans-4,5,6,7-tetrachloro-1-(2,3,4,5tetrachlorophenyl)-2-(trichlorosilyl)-3-((trichlorosilyl)methyl)indane has been determined by x-ray crystallog. The desilylated product, 1,3-cis-4,5,6,7-tetrachloro-1-(2,3,4,5-tetrachloropheny1)-3-((trichlorosily1)methy1)indane, was reduced by LiAlH4, and its structure

was also determined

ACCESSION NUMBER: 2002:582028 CAPLUS

DOCUMENT NUMBER: 137:279236

TITLE: Friedel-Crafts Alkylation of Polychlorobenzenes with

(1,2-Dichloroethyl)trichlorosilane

AUTHOR(S): Han, Joon Soo; Lim, Weon Cheol; Yoo, Bok Ryul; Jin,

Jung-Il; Jung, Il Nam

CORPORATE SOURCE: Organosilicon Chemistry Laboratory, Korea Institute of

Science and Technology, Seoul, 130-650, S. Korea

SOURCE: Organometallics (2002), 21(18), 3803-3809 CODEN: ORGND7; ISSN: 0276-7333

PUBLISHER: American Chemical Society

DOCUMENT TYPE: Journal LANGUAGE: English

OTHER SOURCE(S): CASREACT 137:279236 IT 256343-30-3P 256343-31-4P 464173-81-7P

464173-82-8P 464173-83-9P

RL: SPN (Synthetic preparation); PREP (Preparation)

(preparation of)

RN 256343-30-3 CAPLUS

CN Silane, [2,2-bis(2,5-dichlorophenyl)ethyl]trichloro- (9CI) (CA INDEX NAME)

RN 256343-31-4 CAPLUS

CN Silane, [2,2-bis(2,4-dichlorophenyl)ethyl]trichloro- (9CI) (CA INDEX NAME)

RN 464173-81-7 CAPLUS

CN Silane, [2,2-bis(3,4-dichlorophenyl)ethyl]trichloro- (9CI) (CA INDEX NAME)

$$\begin{array}{c|c} \text{C1} & \\ \text{CH}_2\text{-}\operatorname{SiCl}_3 \\ \\ \text{CH} & \\ \text{CH} & \\ \end{array}$$

RN 464173-82-8 CAPLUS

CN Silane, [2,2-bis(2,3,4-trichlorophenyl)ethyl]trichloro- (9CI) (CA INDEX NAME)

$$\begin{array}{c|c} \text{CH}_2\text{--}\text{SiCl}_3\\ \\ \text{CH}\text{----}\text{R}\\ \\ \text{Cl} \end{array}$$

RN 464173-83-9 CAPLUS

CN Silane, [2,2-bis(2,4,5-trichlorophenyl)ethyl]trichloro- (9CI) (CA INDEX NAME)

$$\begin{array}{c|c} \text{CH}_2\text{--}\text{SiCl}_3 \\ \text{Cl} \\ \text{CH} \\ \text{Cl} \\ \end{array}$$

REFERENCE COUNT:

THERE ARE 41 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

- L3 ANSWER 6 OF 30 CAPLUS COPYRIGHT 2008 ACS on STN
- AB Some mechanistic proposals are made for the competitive desilylation reaction affording the corresponding primary alc. and carboxylic acid that frequently occur in the bioredn. of acylsilanes. C-Si bond cleavage of bioredn. was modeled in reduction of acylsilanes mediated by water in the

presence of montmorillonite K10.

ACCESSION NUMBER: 2000:716174 CAPLUS

DOCUMENT NUMBER: 134:17522

TITLE: A mechanistic study concerning the carbon-silicon bond

cleavage in acylsilane bioreductions

AUTHOR(S): Patrocinio, Amauri F.; Moran, Paulo J. S.

CORPORATE SOURCE: Instituto de Quimcia, Universidade Estraduai de

Campinas, Campinas-SP, 13083-970, Brazil

SOURCE: Journal of Chemical Research, Synopses (2000), (8),

404-405

CODEN: JRPSDC; ISSN: 0308-2342

PUBLISHER: Science Reviews Ltd.

DOCUMENT TYPE: Journal LANGUAGE: English

OTHER SOURCE(S): CASREACT 134:17522

IT 309929-02-0

RL: RCT (Reactant); RACT (Reactant or reagent)

(attempted C-Si bond cleavage reaction mediated by water and

montmorillonite)
309929-02-0 CAPLUS

CN Silane, (diphenylacetyl)trimethyl- (9CI) (CA INDEX NAME)

 $\begin{array}{c} \text{O} \\ || \\ \text{Me}_3 \text{Si-} \text{C--} \text{CHPh}_2 \end{array}$ 

RN

REFERENCE COUNT: 29 THERE ARE 29 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L3 ANSWER 7 OF 30 CAPLUS COPYRIGHT 2008 ACS on STN

AB The oxidative method for the hydrolysis of 1,3-dithianes was applied to 2-silyl-1,3-dithianes by using 4-6 equiv N-bromosuccinimide in aqueous acetone or MeCN, thus providing acylsilanes RCOSiMe3 [R = PhCH2, Ph2CH, Ph, 2-MeOC6H4, 3,4-(MeO)2C6H3, 3,4-(OCH2O)C6H3, 4-ClC6H4, 3-CF3C6H4] with good (40-96%) yields in a short reaction period. The oxidation of aroylsilanes to carboxylic acid was prevented by addition of bases and lowering the reaction

temperature

ACCESSION NUMBER: 2000:545861 CAPLUS

DOCUMENT NUMBER: 134:147633

TITLE: Synthesis of acylsilanes via oxidative hydrolysis of 2-silyl-1,3-dithianes mediated by N-bromosuccinimide

AUTHOR(S): Patrocinio, Amauri F.; Moran, Paulo J. S. CORPORATE SOURCE: Instituto de Quimica, Universidade Estadual de

Campinas, Campinas, Brazil

SOURCE: Journal of Organometallic Chemistry (2000), 603(2),

220-224

CODEN: JORCAI; ISSN: 0022-328X

PUBLISHER: Elsevier Science S.A.

DOCUMENT TYPE: Journal LANGUAGE: English

OTHER SOURCE(S): CASREACT 134:147633

IT 309929-02-0P

RN

RL: SPN (Synthetic preparation); PREP (Preparation)

(preparation of acylsilanes by oxidative hydrolysis of silyldithianes with bromosuccinimide)

309929-02-0 CAPLUS

CN Silane, (diphenylacetyl)trimethyl- (9CI) (CA INDEX NAME)

 $\begin{array}{c} \text{O} \\ || \\ \text{Me}_3 \text{Si-} \text{C--} \text{CHPh}_2 \end{array}$ 

REFERENCE COUNT: 20 THERE ARE 20 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L3 ANSWER 8 OF 30 CAPLUS COPYRIGHT 2008 ACS on STN

AΒ The equilibrium consts. for the ionization of nine stable simple enols and of eight ketones were determined by the ion cyclotron resonance (ICR) method in the gas phase. From these pKa values, seven ketone-enol equilibrium consts. KEnol were calculated The most acidic enol in the series Mes2C:C(OH)R (3) is when R = p-CF3C6H4 ( $\Delta G$  °acid = 323.4 kcal mol-1) and the least acidic one is when R = t-Bu ( $\Delta G$  °acid = 334.7 kcal mol-1). There is a good correlation between the  $\Delta G$  °acid values for the ketones and the enols. For  $4 \alpha$ -aryl-substituted enols (R = Ar) and their keto isomers, there is a rough correlation with Hammett's  $\sigma$  values. The  $\Delta G$  °acid's for the enols where R = Ar correlate linearly with their  $\Delta G$  °acid's in hexane, but other enols deviate from the relationship. The pKa's and pKEnol values were calculated by RHF/3-21G\* and some values were calculated by B3LYP/3-21+G\*. The observed  $\Delta G$  °acid's for the enols give an approx. linear correlation with the calculated  $\Delta E$  °acid values. However, the  $\Delta G$  oeq values for the keto-enol equilibrium in the gas phase or in hexane do not correlate linearly with  $\Delta \text{Eeq}$  for all the enols. The calculated Ar-C:C dihedral angles in the enols 3 change only slightly to modestly on ionization, presumably due to a relatively rigid geometry caused by steric hindrance. The substituent effects on the acidities and the KEnol values are discussed.

ACCESSION NUMBER: 2000:426674 CAPLUS

DOCUMENT NUMBER: 133:237534

TITLE: Acidities and pKEnol values of stable simple enols in

the gas phase

AUTHOR(S): Mishima, Masaaki; Mustanir; Eventova, Irina;

Rappoport, Zvi

CORPORATE SOURCE: Institute for Fundamental Research of Organic

Chemistry, Kyushu University, Fukuoka, 812-8521, Japan

SOURCE: Perkin 2 (2000), (7), 1505-1512 CODEN: PRKTFO; ISSN: 1470-1820

PUBLISHER: Royal Society of Chemistry

DOCUMENT TYPE: Journal LANGUAGE: English

IT 111189-84-5

RL: PRP (Properties)

(acidities and pKEnol values of stable simple enols in gas phase)

RN 111189-84-5 CAPLUS

CN Silane, [bis(2,4,6-trimethylphenyl)acetyl]trimethyl- (9CI) (CA INDEX NAME)

REFERENCE COUNT: 29 THERE ARE 29 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L3 ANSWER 9 OF 30 CAPLUS COPYRIGHT 2008 ACS on STN GI

$$\begin{bmatrix} x^1 \\ x^2 \\ x^3 \\ x^4 \end{bmatrix}_{X^5} \begin{bmatrix} (CH_3)_m \\ (CH_2)_{(y+p)} \\ (CH_2)_{(y+p)} \end{bmatrix}$$

Ι

AB The preparation of aryl substituted alkylsilanes, I (m, p, q = 0, 1; n, y = 0-2; X1, X2, X3, X4, X5 = same or different H, F, C1; R = C1-12 alkyl group; provided that if n = 0, m = 0 and if n = 1, 2, at least two of X1, X2, X3, X4, X5 represent chloro or fluoro group), by the reaction of substituted benzenes with aryl substituted alkylsilanes in the presence of Lewis acid catalysts such as aluminum chloride is described. Thus, aluminum chloride catalyzed alkylation of 1,4-dichlorobenzene with (dichloromethyl)methyldichlorosilane gave 47% [bis(2,5-dichlorophenyl)methyl]methyldichlorosilane.

ACCESSION NUMBER: 2000:96028 CAPLUS

DOCUMENT NUMBER: 132:122758

TITLE: Aryl substituted alkylsilanes and a preparation method

thereof

INVENTOR(S): Jung, Il Nam; Yoo, Bok Ryul; Han, Joon Soo; Cho, Yeon

Seok

PATENT ASSIGNEE(S): Korea Institute of Science and Technology, S. Korea

SOURCE: U.S., 6 pp. CODEN: USXXAM

DOCUMENT TYPE: Patent

LANGUAGE: English

FAMILY ACC. NUM. COUNT: 1

PATENT INFORMATION:

PATENT NO. KIND DATE APPLICATION NO. DATE

US 6022987 A 20000208 US 1997-997583 19971223 PRIORITY APPLN. INFO.: KR 1996-77559 A 19961230

OTHER SOURCE(S): CASREACT 132:122758; MARPAT 132:122758

IT 18419-82-4P 256343-30-3P 256343-31-4P

256343-32-5P

RL: SPN (Synthetic preparation); PREP (Preparation)

(preparation of)

RN 18419-82-4 CAPLUS

CN Silane, trichloro(2,2-diphenylethyl) - (6CI, 8CI, 9CI) (CA INDEX NAME)

Ph<sub>2</sub>CH-CH<sub>2</sub>-SiCl<sub>3</sub>

RN 256343-30-3 CAPLUS

CN Silane, [2,2-bis(2,5-dichlorophenyl)ethyl]trichloro- (9CI) (CA INDEX NAME)

$$\begin{array}{c|c} \text{C1} & \text{CH}_2\text{--}\text{SiCl}_3 \\ \hline & \text{CH} \text{---}\text{R} \\ \hline & \text{C1} \end{array}$$

RN 256343-31-4 CAPLUS

CN Silane, [2,2-bis(2,4-dichlorophenyl)ethyl]trichloro- (9CI) (CA INDEX NAME)

RN 256343-32-5 CAPLUS

CN Silane, [2,2-bis(2,3,4,5-tetrachlorophenyl)ethyl]trichloro- (9CI) (CA INDEX NAME)

REFERENCE COUNT: 10 THERE ARE 10 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L3 ANSWER 10 OF 30 CAPLUS COPYRIGHT 2008 ACS on STN
AB Stable carbocations were prepared at room temperature with benzene as solvent and

tetrakis(pentafluorophenyl)borate (TPFPB) as anion by the addition of solvated triethylsilylium TPFPB or of tributylgermylium TPFPB to 1,1-diphenylethene. These carbocations are stabilized by  $\sigma$  conjugation with nonadjacent Group 14 atoms and resp. constitute stable saturated  $\beta$ -silyl and  $\beta$ -germyl carbocations. NMR parameters, including the 29Si chemical shift, the 13C chemical shifts of the cationic, aryl, and methylene carbons, and the 1-bond 13C-1H coupling constant of the methylene group adjacent to the group 14 element, define the distribution of pos. charge between C and (through  $\sigma$  conjugation) Si or Ge. The extent of hyperconjugation is estimated quant. by comparison with models. The NMR parameters indicate that the cations are open rather than bridged.

ACCESSION NUMBER: 1999:197532 CAPLUS

DOCUMENT NUMBER: 130:338181

TITLE:  $\beta$ -Silyl and  $\beta$ -Germyl Carbocations Stable at

Room Temperature

AUTHOR(S): Lambert, Joseph B.; Zhao, Yan; Wu, Hongwei

CORPORATE SOURCE: Department of Chemistry, Northwestern University,

Evanston, IL, 60208-3113, USA

SOURCE: Journal of Organic Chemistry (1999), 64(8), 2729-2736

CODEN: JOCEAH; ISSN: 0022-3263

PUBLISHER: American Chemical Society

DOCUMENT TYPE: Journal LANGUAGE: English

IT 181220-01-9P, 1,1-Diphenyl-2-(triethylsilyl)ethane RL: SPN (Synthetic preparation); PREP (Preparation)

(preparation of) 181220-01-9 CAPLUS

CN Silane, (2,2-diphenylethyl)triethyl- (9CI) (CA INDEX NAME)

Et3Si-CH2-CHPh2

RN

REFERENCE COUNT: 40 THERE ARE 40 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L3 ANSWER 11 OF 30 CAPLUS COPYRIGHT 2008 ACS on STN

Hydroboration of aliphatic vinyl silanes with the highly electrophilic AΒ bis(pentafluorophenyl)borane, HB(C6F5)2, gives predominantly the thermodynamically favored regioisomer with boron and silicon on the same carbon. Thus, hydroboration of Me3Si(CH2)nCH:CH2 (n = 0, 1, 4) with HB(C6F5)2 in C6D6 gave 94:6 ratio of Me3Si(CH2)nCH2CH2B(C6F5)2 and Me3SiCH{B(C6F5)2}(CH2)nCH3. Thermodn. product mixts. are obtained because equilibration of isomers through boryl migration is facile in the products of hydroboration with HB(C6F5)2. The 1,1-substituted isomers are the most stable by virtue of a ground state  $\beta$ -silicon effect involving hyperconjugation between the Me3Si group and the electrophilic borane center. More complex thermal rearrangements are observed when aromatic vinyl silanes are hydroborated with HB(C6F5)2. Expts. using 13C-labeled and para-substituted substrates provide mechanistic information on these rearrangements which appear to be driven by the formation of compds. which can engage in the ground state  $\beta\text{-silicon}$  interaction. The mechanistic proposals given are supported by computational results performed at the AM1 level.

ACCESSION NUMBER: 1998:801735 CAPLUS

DOCUMENT NUMBER: 130:139386

TITLE: Hydroboration of vinyl silanes with

bis(pentafluorophenyl)borane: ground state

 $\beta$ -silicon effects

AUTHOR(S): Parks, Daniel J.; Piers, Warren E.

CORPORATE SOURCE: Department of Chemistry, University of Calgary,

Calgary, AB, T2N 1N4, Can.

SOURCE: Tetrahedron (1998), 54(51), 15469-15488

CODEN: TETRAB; ISSN: 0040-4020

PUBLISHER: Elsevier Science Ltd.

DOCUMENT TYPE: Journal LANGUAGE: English

OTHER SOURCE(S): CASREACT 130:139386

IT 220082-38-2P

RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)

(preparation and attempted thermal rearrangement of)

RN 220082-38-2 CAPLUS

CN Borane, [2,2-diphenyl-1-(trimethylsilyl)ethyl]bis(pentafluorophenyl)-(9CI) (CA INDEX NAME)

REFERENCE COUNT: 50 THERE ARE 50 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L3 ANSWER 12 OF 30 CAPLUS COPYRIGHT 2008 ACS on STN

AB Hydrosilylation of Ph2C:CH2 with SiCl3 leads in high yields to Ph2CHCH2SiCl3 which was investigated spectroscopically as well as by x-ray structure determination. The compound crystallizes monoclinically in the acentric

space group Cc (a 1002.4, b 1573.8, c 979.7 pm,  $\beta$  106.27°, Z

4). The bonding parameters show no special features. By fluorination

with ZnF2 in Et2O and by reduction with "Red-Al" in toluene, the corresponding

SiF3 and SiH3 derivs. were resp. prepared ACCESSION NUMBER: 1997:499876 CAPLUS

DOCUMENT NUMBER: 127:190784

TITLE: Syntheses of 2,2-diphenylethyl-substituted silanes.

Molecular structure of trichloro-(2,2-

diphenylethyl)silane

AUTHOR(S): Dautel, J.; Abele, S.; Schwarz, W.

CORPORATE SOURCE: Institut Anorganische Chemie, Universitat Stuttgart,

Stuttgart, D-70569, Germany

SOURCE: Zeitschrift fuer Naturforschung, B: Chemical Sciences

(1997), 52(7), 778-784

CODEN: ZNBSEN; ISSN: 0932-0776

PUBLISHER: Verlag der Zeitschrift fuer Naturforschung

DOCUMENT TYPE: Journal LANGUAGE: German

OTHER SOURCE(S): CASREACT 127:190784

IT 194288-10-3P 194288-11-4P

RL: SPN (Synthetic preparation); PREP (Preparation)

(preparation of) 194288-10-3 CAPLUS

CN Silane, (2,2-diphenylethyl)trifluoro- (9CI) (CA INDEX NAME)

Ph2CH-CH2-SiF3

RN

RN 194288-11-4 CAPLUS

CN Silane, (2,2-diphenylethyl) - (9CI) (CA INDEX NAME)

Ph<sub>2</sub>CH-CH<sub>2</sub>-SiH<sub>3</sub>

IT 18419-82-4P

RL: PRP (Properties); RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)

(preparation, crystal structure, reduction and fluorination of)

RN 18419-82-4 CAPLUS

CN Silane, trichloro(2,2-diphenylethyl) - (6CI, 8CI, 9CI) (CA INDEX NAME)

Ph<sub>2</sub>CH-CH<sub>2</sub>-SiCl<sub>3</sub>

L3 ANSWER 13 OF 30 CAPLUS COPYRIGHT 2008 ACS on STN

AB Preparation is described of an active, selective and stable heterogenized hydrosilylation platinum catalyst. The catalyst is prepared by (1) modification of a silica carrier with a silane compound (RO)3Si(CH2)n[NH(CH2)m]xNH2 or its mixture with (OR)3Si(CH)2nR1 (R = Me, Et, n,m = 1-3, x = 0, 1; R1 = thiol, diphenylphosphine), (2) deposition of Pt complex by immobilizing hexachloroplatinic acid, and (3) coupling with (meth)acrylic acid in presence of R2N=C=NR2 (R2 = cyclohexyl, isopropyl). The polymer membrane produced by condensation of the surface amino groups with (meth)acrylic acid prevents elution of the Pt complex in the catalytic process. The obtained catalyst show high constant activity for apprx.300 h in gas-phase hydrosilylation of acetylene with trichlorosilane.

ACCESSION NUMBER: 1996:636936 CAPLUS

DOCUMENT NUMBER: 125:258084

TITLE: Heterogenized platinum catalyst and its preparation

method

INVENTOR(S): Marciniec, Bogdan; Foltynowicz, Zenon; Lewandowski,

Mariusz

PATENT ASSIGNEE(S): Uniwersytet Im Adama Mickiewicza, Pol.

SOURCE: Pol., 6 pp. CODEN: POXXA7

DOCUMENT TYPE: Patent LANGUAGE: Polish

FAMILY ACC. NUM. COUNT: 1

PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PL 169330	В1	19960731	PL 1992-295178	19920706
PRIORITY APPLN. INFO.:			PL 1992-295178	19920706

IT 182414-79-5

RL: RCT (Reactant); RACT (Reactant or reagent)

(preparation of heterogenized hydrosilylation platinum catalyst)

RN 182414-79-5 CAPLUS

CN Silane, (2,2-diphenylethyl)triethoxy- (9CI) (CA INDEX NAME)

L3 ANSWER 14 OF 30 CAPLUS COPYRIGHT 2008 ACS on STN

AB Diphenyl[(triethylsilyl)methyl]methylium tetrakis(pentafluorophenyl)borate , a  $\beta$ -silyl-stabilized carbocation (Et3SiCH2CPh2+), was prepared in aromatic solvents by the addition of triethylsilylium tetrakis(pentafluorophenyl)borate to 1,1-diphenylethene. The 13C resonance position of the phenyl-substituted C occurs at  $\delta$  225.4 and indicates that the predominance of pos. charge resides on C. The single peak in the 29Si spectrum at  $\delta$  46.2 is consistent with some pos. charge on Si through hyperconjugation. The NMR spectra are in agreement

with an open structure rather than a three-membered ring with bridging Si.

ACCESSION NUMBER: 1996:486171 CAPLUS

DOCUMENT NUMBER: 125:221940

TITLE: A Stable  $\beta$ -Silyl Carbocation AUTHOR(S): Lambert, Joseph B.; Zhao, Yan

CORPORATE SOURCE: Department of Chemistry, Northwestern University,

Evanston, IL, 60208, USA

SOURCE: Journal of the American Chemical Society (1996),

118(33), 7867-7868

CODEN: JACSAT; ISSN: 0002-7863

PUBLISHER: American Chemical Society

DOCUMENT TYPE: Journal LANGUAGE: English

IT 181220-01-9P, (2,2-Diphenylethyl)triethylsilane
RL: SPN (Synthetic preparation); PREP (Preparation)

(formation by trapping  $\beta$ -silyl carbocation with silane)

RN 181220-01-9 CAPLUS

CN Silane, (2,2-diphenylethyl)triethyl- (9CI) (CA INDEX NAME)

L3 ANSWER 15 OF 30 CAPLUS COPYRIGHT 2008 ACS on STN

Meso- and racemic-1,2-diethyl-1,2-dimethyldiphenyldisilane (2a) and (2b) AB were synthesized resp. by hydrogenation of meso- and racemic-1,2-diethynyl-1,2-dimethyldiphenyldisilane in the presence of a IrCl(CO)(PPh3)2 catalyst. Irradiation of 2a with a low-pressure Hg lamp in the presence of isobutene in hexane proceeded with high diastereospecificity to give (R,S) - and (S,R) -2-(isobutylethylmethylsilyl)-1-(ethylmethylphenylsilyl)benzene in 77% yield. Similar irradiation of 2b with isobutene produced (R,R) - and (S,S) -isomer. The photolysis of 2a and 2b in the presence of 1,1-diphenylethylene also proceeded diastereospecifically to give the resp. adducts. With 2,3-dimethylbutadiene, 2a and 2b produced the corresponding adducts, whose spectrometric anal. showed two diastereomers. Results on theor. studies which were carried out using PhSiH2SiH3 as a model also are reported. The crystal and mol. structures of racemic-1,2-diethynyl-1,2dimethyldiphenyldisilane and o-(ethylmethylphenylsilyl)(ethylmethyl(2,2diphenylethyl)silyl)benzene were determined by x-ray crystallog.

ACCESSION NUMBER: 1996:394105 CAPLUS

DOCUMENT NUMBER: 125:114750

TITLE: Silicon-Carbon Unsaturated Compounds. 57. Photolysis

of meso- and racemic-1,2-Diethyl-1,2-

dimethyldiphenyldisilane, Direct Evidence for a Concerted 1,3-Silyl Shift to ortho-Carbon in the

Phenyl Ring

AUTHOR(S): Ohshita, Joji; Niwa, Hiroyuki; Ishikawa, Mitsuo;

Yamabe, Tokio; Yoshii, Takao; Nakamura, Kouichi

CORPORATE SOURCE: Faculty of Engineering, Hiroshima University,

Higashi-Hiroshima, 724, Japan

SOURCE: Journal of the American Chemical Society (1996),

118(29), 6853-6859

CODEN: JACSAT; ISSN: 0002-7863

PUBLISHER: American Chemical Society

DOCUMENT TYPE: Journal LANGUAGE: English

IT 179233-69-3P

RL: SPN (Synthetic preparation); PREP (Preparation)

(racemic)

RN 179233-69-3 CAPLUS

CN Silane, (2,2-diphenylethyl)ethyl[2-(ethylmethylphenylsilyl)phenyl]methyl-, (R\*,S\*)- (9CI) (CA INDEX NAME)

Relative stereochemistry.

IT 179233-71-7P

RL: PRP (Properties); SPN (Synthetic preparation); PREP (Preparation) (racemic; preparation and crystal structure of)

RN 179233-71-7 CAPLUS

CN Silane, (2,2-diphenylethyl)ethyl[2-(ethylmethylphenylsilyl)phenyl]methyl-, (R\*,R\*)- (9CI) (CA INDEX NAME)

Relative stereochemistry.

L3 ANSWER 16 OF 30 CAPLUS COPYRIGHT 2008 ACS on STN

AB Tellurol esters having an anion stabilizing group at the position  $\alpha$ to the carbonyl, such as aryl-, (phenylthio)-, and (benzyloxy) ethanetelluroates, gave enol silyl ethers of the corresponding acylsilanes in good to excellent yields upon treatment with 2 equiv BuLi in the presence of chlorosilanes. This reaction was stereoselective, and Z-isomers were obtained as sole or major products from a variety of chlorosilanes, such as trimethyl-, triethyl-, dimethylphenyl-, and tert-butyldimethylsilyl chlorides. Control expts. revealed that the reaction comprises the following consecutive processes: (i)  $\alpha$ -proton abstraction, (ii) chlorosilane-trapping, (iii) Li-Te exchange, (i.v.) 1,2-silyl migration, and (v) chlorosilane-trapping. Intramol. rearrangement of  $(\alpha$ -siloxyvinyl)lithiums to Li enolates (step i.v.) was very fast even at  $-105^{\circ}$ , and the former could not be trapped intermolecularly with either HOAc or with coexisting trimethylsilyl chloride.

ACCESSION NUMBER: 1995:229646 CAPLUS

DOCUMENT NUMBER: 122:81481

ORIGINAL REFERENCE NO.: 122:15487a, 15490a

TITLE: Conversion of Tellurol Esters to Enol Silyl Ethers of

Acylsilanes

AUTHOR(S): Inoue, Toru; Kambe, Nobuaki; Ryu, Ilhyong; Sonoda,

Noboru

CORPORATE SOURCE: Faculty of Engineering, Osaka University, Suita,

SUITA, Japan

SOURCE: Journal of Organic Chemistry (1994), 59(26), 8209-14

CODEN: JOCEAH; ISSN: 0022-3263

PUBLISHER: American Chemical Society

DOCUMENT TYPE: Journal LANGUAGE: English

OTHER SOURCE(S): CASREACT 122:81481

IT 160463-58-1P

RL: SPN (Synthetic preparation); PREP (Preparation)

(conversion of tellurol esters to silyl enol ethers of acylsilanes)

RN 160463-58-1 CAPLUS

CN Silane, (1,1-dimethylethyl)(diphenylacetyl)dimethyl- (9CI) (CA INDEX NAME)

L3 ANSWER 17 OF 30 CAPLUS COPYRIGHT 2008 ACS on STN

AB The replacement of the usual electron donating alkyl groups on silicon,

with electroneg. chloride ligands, changes the mechanism and outcome of the reaction of (E)- $\beta$ -(dichlorobenzylsily1)styrene with proton and carbon electrophiles. Electrophilic addition rather than the usual substitution occurs, so that the silicon remains intact to mediate further chemical reactions. The exptl. results show that Friedel-Crafts reactions of the silylated alkene are subject to the same limitations observed for non-silylated alkenes; the extent of polymerization increases as the stability

of the carbenium ion decreases.

ACCESSION NUMBER: 1994:509734 CAPLUS

DOCUMENT NUMBER: 121:109734

ORIGINAL REFERENCE NO.: 121:19853a, 19856a

TITLE: Electrophilic addition to styrylsilanes: sequential

carbon-carbon bond forming reactions

AUTHOR(S): Henry, Courtney; Jueschke, Ralf; Brook, Michael A.

CORPORATE SOURCE: Department of Chemistry, McMaster University,

Hamilton, ON, L8S 4M1, Can.

SOURCE: Inorganica Chimica Acta (1994), 220(1-2), 145-54

CODEN: ICHAA3; ISSN: 0020-1693

DOCUMENT TYPE: Journal LANGUAGE: English

IT 156970-66-0P 156970-67-1P 156970-68-2P

156970-69-3P

RL: PRP (Properties); SPN (Synthetic preparation); PREP (Preparation)

(preparation and NMR spectra of)

RN 156970-66-0 CAPLUS

CN Silane, trichloro[2-(2-methylphenyl)-2-phenylethyl]- (9CI) (CA INDEX

NAME)

RN 156970-67-1 CAPLUS

CN Silane, trichloro[2-(4-methylphenyl)-2-phenylethyl]- (9CI) (CA INDEX NAME)

RN 156970-68-2 CAPLUS

CN Silane, [1-[(2-methylphenyl)phenylmethyl]-2-phenyl-1,3-propanediyl]bis[trichloro- (9CI) (CA INDEX NAME)

156970-69-3 CAPLUS RN

CN Silane, [1-[(4-methylphenyl)phenylmethyl]-2-phenyl-1,3propanediyl]bis[trichloro- (9CI) (CA INDEX NAME)

L3 ANSWER 18 OF 30 CAPLUS COPYRIGHT 2008 ACS on STN GΙ

Photochem. decomposition of (1-diazo-2-oxoalkyl)silanes R1COCN2SiR3 [I: SiR3 = AB SiEt3, Si(CHMe2)3, Me3CSiMe2, Ph2SiCMe3, (Me3C)2SiMe; R1 = Me, CMe3, CHPh2, 1-adamantyl, Ph] results in Wolff rearrangement yielding silyl ketenes R3SiCR1:C:O. From I [SiR3 = Me2SiCMe3, MeSi(CMe3)2, Ph2SiCMe3, Si(CHMe2)3, R1 = CMe3], 2-silyl-cyclobutanones are formed as byproducts, arising from intramol. C/H insertion of the acyl carbene intermediate. Irradiation of diazotriisopropylsilylacetamide yields only  $\beta$ -lactam II and  $\gamma$ -lactam III. Wolff rearrangement also takes place on copper triflate catalyzed decomposition of I whereas the 1-oxa-2-sila-4-cyclopentene IV is obtained from I [R3Si = (Me2CH)3Si, R1 = CMe3], probably as the result of SiC/H insertion of a copper carbene intermediate.

ACCESSION NUMBER: 1990:217024 CAPLUS

DOCUMENT NUMBER: 112:217024

ORIGINAL REFERENCE NO.: 112:36649a,36652a

TITLE: Wolff rearrangement of (1-diazo-2-oxoalkyl)silanes AUTHOR(S): Brueckmann, Ralf; Schneider, Klaus; Maas, Gerhard

CORPORATE SOURCE: Fachbereich Chem., Univ. Kaiserslautern, Kaiserslautern, D-6750, Fed. Rep. Ger. Tetrahedron (1989), 45(17), 5517-30 SOURCE:

CODEN: TETRAB; ISSN: 0040-4020

DOCUMENT TYPE: Journal LANGUAGE: English

OTHER SOURCE(S): CASREACT 112:217024

IT 126364-86-1P 126364-87-2P

RL: SPN (Synthetic preparation); PREP (Preparation)

(preparation of) 126364-86-1 CAPLUS

CN 1-Propen-1-one, 3,3-diphenyl-2-[tris(1-methylethyl)silyl]- (CA INDEX

NAME)

RN

RN 126364-87-2 CAPLUS

CN Benzenepropanoic acid,  $\beta$ -phenyl- $\alpha$ -[tris(1-methylethyl)silyl]- (CA INDEX NAME)

Si(Pr-i)3 | HO<sub>2</sub>C-CH-CHPh<sub>2</sub>

L3 ANSWER 19 OF 30 CAPLUS COPYRIGHT 2008 ACS on STN

AB MO calcns. suggest that replacement of an  $\alpha$ -Me by an  $\alpha$ -silyl substituent will increase the stability of the enols H2C:C(OH)R compared with their keto isomers H3CCOR. This is corroborated by the synthesis of the stable enol (Mes)2C:C(OH)R (Mes = mesityl, R = SiMe3) which does not ketonize in hexane/CF3CO2H although the analog with R = CMe3 is converted almost completely to the ketone under the same conditions.

ACCESSION NUMBER: 1988:94631 CAPLUS

DOCUMENT NUMBER: 108:94631

ORIGINAL REFERENCE NO.: 108:15575a,15578a

TITLE: The first  $\alpha$ -silicon-substituted simple enol. The stabilizing effect of the silyl substituent

AUTHOR(S): Nadler, Ella B.; Rappoport, Zvi; Arad, Dorit; Apeloig,

Yitzhak

CORPORATE SOURCE: Dep. Org. Chem., Hebrew Univ., Jerusalem, 91904,

Israel

SOURCE: Journal of the American Chemical Society (1987),

109(25), 7873-5

CODEN: JACSAT; ISSN: 0002-7863

DOCUMENT TYPE: Journal LANGUAGE: English

OTHER SOURCE(S): CASREACT 108:94631

IT 111189-84-5 111189-85-6

RL: RCT (Reactant); RACT (Reactant or reagent)

(keto-enol equilibrium consts. for)

RN 111189-84-5 CAPLUS

CN Silane, [bis(2,4,6-trimethylphenyl)acetyl]trimethyl- (9CI) (CA INDEX NAME)

RN 111189-85-6 CAPLUS

CN Silane, [bis(2,4,6-trimethylphenyl)acetyl]- (9CI) (CA INDEX NAME)

L3 ANSWER 20 OF 30 CAPLUS COPYRIGHT 2008 ACS on STN

AB The reaction of Cl3SiCH:CHCl, Me2SiClCH:CHCl, Me3SiCH:CHCl and Cl3SiC.tplbond.CH with protonating compds., Mg, hydrosilanes, C6H6 and adamantane was studied. Thus, heating Cl3SiCH:CHCl with adamantane in the presence of AlCl3 gave 26% Cl3SiCH2CH2R (R = 1-admantyl).

ACCESSION NUMBER: 1984:491036 CAPLUS

DOCUMENT NUMBER: 101:91036

ORIGINAL REFERENCE NO.: 101:13963a,13966a

TITLE: Some chemical properties of chlorovinyl- and

ethynylsilanes

AUTHOR(S): Sheludyakov, V. D.; Zhun, V. I.; Lakhtin, V. G.;

Bochkarev, V. N.; Slyusarenko, T. F.; Nosova, V. N.;

Kisin, A. V.

CORPORATE SOURCE: USSR

SOURCE: Zhurnal Obshchei Khimii (1984), 54(3), 640-6

CODEN: ZOKHA4; ISSN: 0044-460X

DOCUMENT TYPE: Journal LANGUAGE: Russian

OTHER SOURCE(S): CASREACT 101:91036

IT 18419-82-4P

RN

RL: SPN (Synthetic preparation); PREP (Preparation)

(preparation of) 18419-82-4 CAPLUS

CN Silane, trichloro(2,2-diphenylethyl) - (6CI, 8CI, 9CI) (CA INDEX NAME)

Ph<sub>2</sub>CH-CH<sub>2</sub>-SiCl<sub>3</sub>

L3 ANSWER 21 OF 30 CAPLUS COPYRIGHT 2008 ACS on STN

AB Under the agency of the potent lithiating agent, BuLi in Me2N(CH2)2NMe2, an array of organosilanes was found to undergo 1,n-silyl rearrangements via carbanionic intermediates. Unambiguous 1,2-, 1,3- and 1,4-silyl

shifts were uncovered in 1-trimethylsilyl-1,1,2-triphenylethane, 1,1-bis(trimethylsilyl)-1-phenylalkanes and 1,2-bis(trimethylsilyl)-1,2-diphenylethane, resp. Cross-over and competition expts. established that these rearrangements generally are intramol. and occur with decreasing ease in the order, 1,2 > 1,3 » 1,4. In other compds., such as 1,1-bis(trimethylsilyl)-1,2-diphenylethane, 1,n-bis(trimethylsilyl) benzenes and triphenyl(trimethylsilyl) methane, competing 1,n-silyl shifts occurred. Attack of the organolithium intermediates on solvent and Si-Li exchange were significant side reactions in some instances. 1-Trimethylgermyl-1,1,2-triphenylgermane underwent no discernible rearrangement but rather gave the product expected from Ge-Li exchange. By conducting time and competition studies, it was shown that lithiation is the product-determining step in these rearrangements and that dual pathways, namely 1,3- vs. consecutive 1,2- and 1,4-pathways, are operative in certain rearrangements.

ACCESSION NUMBER: 1982:142942 CAPLUS

DOCUMENT NUMBER: 96:142942

ORIGINAL REFERENCE NO.: 96:23517a,23520a

TITLE: Organosilicon compounds with functional groups

proximate to silicon. Part 15. 1,n-Triorganosilyl migrations in the rearrangements of silyl-substituted

organolithium compounds

AUTHOR(S): Eisch, John J.; Tsai, Miin Rong

CORPORATE SOURCE: Dep. Chem., State Univ. New York, Binghamton, NY,

13901, USA

SOURCE: Journal of Organometallic Chemistry (1982), 225(1),

5-23

CODEN: JORCAI; ISSN: 0022-328X

DOCUMENT TYPE: Journal LANGUAGE: English

OTHER SOURCE(S): CASREACT 96:142942

IT 81290-08-6

RL: RCT (Reactant); RACT (Reactant or reagent)

(attempted rearrangement of, in presence of butyllithium)

RN 81290-08-6 CAPLUS

CN Silane, trimethyl(1,2,2-triphenylethyl)- (9CI) (CA INDEX NAME)

Ph | Me3Si-CH-CHPh2

IT 81290-12-2P

RN 81290-12-2 CAPLUS

CN Silane, ethyldimethyl(1,2,2-triphenylethyl)- (9CI) (CA INDEX NAME)

Me Ph | | Et-Si-CH-CHPh<sub>2</sub> Me

L3 ANSWER 22 OF 30 CAPLUS COPYRIGHT 2008 ACS on STN

AB Ten acyclic, cyclic and aralkylated silanes were treated with Ph3C+ BF4- in CH2Cl2 to measure rates of oxidative desilylation: RCH2CH2SiR3 + Ph3C+ BF4-  $\rightarrow$  Ph3CH + RCH:CH2 + R3SiF + BF3. The divergence of rates,

from Ph2CHCH2SiMe3 (which was inert) through dimethylsilacyclopentane (k2 = 4 + 10-6) to dimethylsilacyclohexane (k2 = 2.2 + 10-3), can not be rationalized on purely electronic grounds. A transition state requiring anticoplanar arrangement of the Si moiety and  $\beta$ -H to be extruded is proposed. Dimethylsilacyclobutane, which reacts extremely rapidly (k2  $\approx$  2 + 10-2), suffers allylic cleavage of the initially formed CH2:CHCH2SiMe2F. As the olefin products suffer decomposition or polymerization under the reaction conditions, this desilylation is of minimal

preparative value.

ACCESSION NUMBER: 1981:83236 CAPLUS

DOCUMENT NUMBER: 94:83236

ORIGINAL REFERENCE NO.: 94:13561a,13564a

TITLE: Oxidative desilylation of alkylsilanes with

triphenylcarbenium ion. Control by transition-state

geometry

AUTHOR(S): Washburne, Stephen S.; Szendroi, Robert

CORPORATE SOURCE: Dep. Chem., Temple Univ., Philadelphia, PA, 19122, USA

SOURCE: Journal of Organic Chemistry (1981), 46(4), 691-3

CODEN: JOCEAH; ISSN: 0022-3263

DOCUMENT TYPE: Journal LANGUAGE: English

IT 75961-63-6 75961-64-7

RL: RCT (Reactant); RACT (Reactant or reagent)

(reaction of, with triphenylcarbenium tetrafluoroborate, kinetics of)

RN 75961-63-6 CAPLUS

CN Silane, (2,2-diphenylethyl)trimethyl- (9CI) (CA INDEX NAME)

Ph<sub>2</sub>CH-CH<sub>2</sub>-SiMe<sub>3</sub>

RN 75961-64-7 CAPLUS

CN Silane, (2,2-diphenylethyl)diethylmethyl- (9CI) (CA INDEX NAME)

$$\begin{array}{c} \text{Me} \\ | \\ \text{Et-Si-CH}_2\text{-CHPh}_2 \\ | \\ \text{Et} \end{array}$$

L3 ANSWER 23 OF 30 CAPLUS COPYRIGHT 2008 ACS on STN GI

AB Cyclosiloxanes I (R = PhCH2CH2, Ph2CHCH2, CHPhCH2Ph, CPh:CHPh) were prepared in 41.2-71% yields by condensation of RSiCl2Me with (HOSiMe2)20. Similarly obtained was 66.3% II. Condensation of RSi(OH)2Me with

(ClPhMeSi) 20 gave 55.9-72.9% III.

ACCESSION NUMBER: 1978:509707 CAPLUS

DOCUMENT NUMBER: 89:109707

ORIGINAL REFERENCE NO.: 89:16921a,16924a

TITLE: Synthesis of organosiloxanes with aliphatic-aromatic

radicals at the silicon atom

AUTHOR(S): Nogaideli, A. I.; Nakaidze, L. I.; Tskhovrebashvili,

V.S.

CORPORATE SOURCE: Tbilis. Gos. Univ., Tiflis, USSR

SOURCE: Zhurnal Obshchei Khimii (1978), 48(6), 1344-7

CODEN: ZOKHA4; ISSN: 0044-460X

DOCUMENT TYPE: Journal LANGUAGE: Russian

OTHER SOURCE(S): CASREACT 89:109707

IT 57522-91-5

RL: RCT (Reactant); RACT (Reactant or reagent)

(reaction of, with dichlorodiphenyldimethyldisiloxane)

RN 57522-91-5 CAPLUS

CN Silanediol, (2,2-diphenylethyl)methyl- (9CI) (CA INDEX NAME)

$$\begin{array}{c} \text{OH} \\ \mid \\ \text{Me-Si-CH}_2\text{-CHPh}_2 \\ \mid \\ \text{OH} \end{array}$$

IT 53888-97-4

RL: RCT (Reactant); RACT (Reactant or reagent) (reaction of, with dihydroxytetramethyldisiloxane)

RN 53888-97-4 CAPLUS

CN Silane, dichloro(2,2-diphenylethyl) methyl- (9CI) (CA INDEX NAME)

$$\begin{array}{c|c} \text{Cl} & \\ | \\ \text{Me-Si-CH}_2\text{-CHPh}_2 \\ | \\ \text{Cl} \end{array}$$

L3 ANSWER 24 OF 30 CAPLUS COPYRIGHT 2008 ACS on STN

GI For diagram(s), see printed CA Issue.

AB Alkaline hydrolysis of RR1SiCl2 gave RR1Si(OH)2 (R = PhCH2CHPh, Ph2CHCH2; R1 = Me, Et) in 68.7-81-6% yields. Hydrolytic polycondensation of RSiCl3 in H2O-Me2CO at  $-5^\circ$  gave I (R = Ph2CHCH2, PhCH2CHPh, PhCH:CPh) whereas

in basic ether or H2O-ether-NaOH solns., cyclopolysiloxanes were formed.

ACCESSION NUMBER: 1976:31176 CAPLUS

DOCUMENT NUMBER: 84:31176
ORIGINAL REFERENCE NO.: 84:5109a,5112a

TITLE: Hydrolysis of aliphatic-aromatic di- and

trichlorosilanes

AUTHOR(S): Andrianov, K. A.; Nogaideli, A. I.; Tskhovrebashvili,

V. S.; Nakaidze, L. I.; Zhinkin, D. Ya.

CORPORATE SOURCE: Tbilis. Gos. Univ., Tiflis, USSR

SOURCE: Doklady Akademii Nauk SSSR (1975), 223(3), 603-5

[Chem]

CODEN: DANKAS; ISSN: 0002-3264

DOCUMENT TYPE: Journal LANGUAGE: Russian IT 18419-82-4 53888-97-4 53888-98-5

RL: RCT (Reactant); RACT (Reactant or reagent)

(alkaline hydrolysis of)

RN 18419-82-4 CAPLUS

CN Silane, trichloro(2,2-diphenylethyl)- (6CI, 8CI, 9CI) (CA INDEX NAME)

Ph<sub>2</sub>CH-CH<sub>2</sub>-SiCl<sub>3</sub>

RN 53888-97-4 CAPLUS

CN Silane, dichloro(2,2-diphenylethyl)methyl- (9CI) (CA INDEX NAME)

$$\begin{array}{c|c} & \text{Cl} \\ | \\ \text{Me-Si-CH}_2\text{-CHPh}_2 \\ | \\ \text{Cl} \end{array}$$

RN 53888-98-5 CAPLUS

CN Silane, dichloro(2,2-diphenylethyl)ethyl- (9CI) (CA INDEX NAME)

$$\begin{array}{c|c} \texttt{C1} & \\ | \\ \texttt{Et-Si-CH}_2 - \texttt{CHPh}_2 \\ | \\ \texttt{C1} \end{array}$$

IT 57522-91-5P 57522-92-6P

RL: SPN (Synthetic preparation); PREP (Preparation)

```
(preparation of)
     57522-91-5 CAPLUS
RN
CN
     Silanediol, (2,2-diphenylethyl) methyl- (9CI) (CA INDEX NAME)
    ОН
Me-Si-CH2-CHPh2
    ОН
RN
     57522-92-6 CAPLUS
CN
     Silanediol, (2,2-diphenylethyl)ethyl- (9CI) (CA INDEX NAME)
    ОН
Et-Si-CH2-CHPh2
    ОН
     ANSWER 25 OF 30 CAPLUS COPYRIGHT 2008 ACS on STN
     The hydrosilylation of Ph2C:CH2 and PhCH:CHPh with RSiHCl2 gave
     Ph2CHCH2SiRCl2 and PhCH2CHPhSiRCl2, resp. (R = Cl, Me, Et, Ph).
ACCESSION NUMBER:
                         1974:569584 CAPLUS
DOCUMENT NUMBER:
                          81:169584
ORIGINAL REFERENCE NO.: 81:26243a,26246a
                         Hydrosilylation of isomeric diphenylethylenes
TITLE:
                         Nogaideli, A. I.; Nakaidze, L. I.; Tskhovrebashvili,
AUTHOR(S):
                         V. S.
CORPORATE SOURCE:
                          Tbilis. Gos. Univ., Tbilisi, USSR
SOURCE:
                          Zhurnal Obshchei Khimii (1974), 44(8), 1763-6
                         CODEN: ZOKHA4; ISSN: 0044-460X
DOCUMENT TYPE:
                         Journal
LANGUAGE:
                         Russian
     18419-82-4P 53888-97-4P 53888-98-5P
     RL: SPN (Synthetic preparation); PREP (Preparation)
        (preparation of)
RN
     18419-82-4 CAPLUS
CN
     Silane, trichloro(2,2-diphenylethyl)- (6CI, 8CI, 9CI) (CA INDEX NAME)
Ph<sub>2</sub>CH-CH<sub>2</sub>-SiCl<sub>3</sub>
RN
     53888-97-4 CAPLUS
CN
     Silane, dichloro(2,2-diphenylethyl)methyl- (9CI) (CA INDEX NAME)
   C1
Me-Si-CH2-CHPh2
   C1
     53888-98-5 CAPLUS
RN
```

Silane, dichloro(2,2-diphenylethyl)ethyl- (9CI) (CA INDEX NAME)

CN

$$\begin{array}{c|c} \mathtt{C1} & \\ | \\ \mathtt{Et-Si-CH}_2-\mathtt{CHPh}_2 \\ | \\ \mathtt{C1} \end{array}$$

53888-99-6 CAPLUS RN

CN Silane, dichloro(2,2-diphenylethyl)phenyl- (9CI) (CA INDEX NAME)

$$\begin{array}{c|c} \mathtt{C1} & \\ | \\ \mathtt{Ph-Si-CH_2-CHPh_2} \\ | \\ \mathtt{C1} \end{array}$$

L3 ANSWER 26 OF 30 CAPLUS COPYRIGHT 2008 ACS on STN

AΒ Triarylsilylmethyl-metallic reagents were prepared by several routes: metalation; addition of PhLi to vinyltriphenylsilane; direct synthesis; and by halogen-metal exchange. The latter method is highly superior as regards both generality of application and yields. Dibromo-methylsilanes undergo halogen-metal exchange at  $-78^{\circ}$ , and reaction of the product with HBr serves as a valuable way of converting geminal dibromides to monobromides. The organometallic reagents were characterized in several ways, especially by carbonation to give the related carboxylic acid.

ACCESSION NUMBER: 1970:100816 CAPLUS

DOCUMENT NUMBER: 72:100816

ORIGINAL REFERENCE NO.: 72:18304h,18305a

TITLE:

Preparation and reactions of

triarylsilylmethylmetallic reagents AUTHOR(S):

Brook, Adrian G.; Duff, J. M.; Anderson, David Gordon

CORPORATE SOURCE: Dep. Chem., Univ. Toronto, Toronto, ON, Can.

SOURCE: Canadian Journal of Chemistry (1970), 48(4), 561-9

CODEN: CJCHAG; ISSN: 0008-4042

DOCUMENT TYPE: Journal LANGUAGE: English

ΙT 18834-21-4P

RL: SPN (Synthetic preparation); PREP (Preparation)

(preparation of)

18834-21-4 CAPLUS RN

Silane, (2,2-diphenylethyl)triphenyl- (6CI, 8CI) (CA INDEX NAME) CN

Ph3Si-CH2-CHPh2

ANSWER 27 OF 30 CAPLUS COPYRIGHT 2008 ACS on STN L3

Ph3SiK (I) and Ph3SiLi (II) added to the olefinic linkage of 1,1-diphenylethylene (III) and of triphenylethylene (IV). No addition occurred, under corresponding conditions, to tetraphenylethylene ( $\mathbf{V}$ ) and to a variety of aliphatic and alicyclic olefins. For comparison purposes, triphenyl(1,1-diphenylethyl)silane (VI) and triphenyl(1,1,2triphenylethyl)silane (VII) were synthesized by metalation of triphenyl(diphenylmethyl)silane (VIII) with BuLi and subsequent treatment with Me2SO4 and PhCH2Cl (IX), resp. I suspension (from cleavage of 0.01 mole hexaphenyldisilane) left 2 hrs. with 3.6 g. III in 20 ml. Et2O, the

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mixture hydrolyzed, the solution dried, and Et20 evaporated gave 3.5 g.
     triphenyl(2,2-diphenylethyl)silane (X), lustrous plates, m. 106-8^{\circ}
     (alc.). II (0.0122 mole) in tetrahydrofuran (THF) added to 2.2 g. III,
     the mixture stirred 0.5 hr. at room temperature, then hydrolyzed, the organic
layer
     evaporated, and the residue recrystd. gave 80% X. Ph2CHCH2Cl (4.3 g.) in 20
     ml. Et20 added during 2 min. to an amalgamated suspension of 0.02 mole I,
     the mixture left 2 hrs., hydrolyzed, and the product isolated gave 1.1 q.
     hexaphenyldisilane. The Et20 solution on evaporation gave 4.1 g. X. PhLi
     mole) in THF added to 0.5 g. triphenyl-\beta-styrylsilane, stirred 2 hrs.
     at room temperature, the mixture hydrolyzed, Et20 added, the solvent removed,
and
     the residue chromatographed on Al2O3 gave 0.18 g. Ph4Si. No other product
     was isolated from the mother liquor. BuLi (0.015 \text{ mole}) added at once to 5
     g. VIII in 25 ml. THF, the solution stirred 40 min. at room temperature, excess
     Me2SO4 added, then hydrolyzed, and the product separated gave 58% VI, m.
     193-5° (C6H6-alc.). II (0.020 mole) in THF added to 5.12 g. IV,
     the mixture stirred 1 hr. at room temperature, hydrolyzed, and the organic
layer
     worked up as usual gave 6.4 g. 1,2,2-isomer of VII, m. 171-2°
     (C6H6-alc.). BuLi (0.015 mole) added to 5 g. VIII in 25 ml. THF, stirred
     40 min. at room temperature, excess IX added, the mixture hydrolyzed, and
     up gave 1.5 g. VII, m. 198-200° (C6H6-alc.). II (0.015 mole) in
     THF stirred 6 hrs. at room temperature with 5 q. V, then 1 hr. at 50°,
     hydrolyzed with dilute acid, and the organic portion worked up gave 4.2~\mathrm{g}. V,
     m. 222-4°; the filtrate chromatographed gave 2.2 g. Ph3SiH, m.
     43-5^{\circ} (MeOH). Attempted reactions of I with other olefins were
     carried out by mixing a suspension of I with an equimolar amount of the
     olefinic compound; the mixture stirred a certain time, H2O added, the organic
    layer dried, evaporated, and the residue crystallized gave triphenylsilanol
(XI) as
     chief product. In 2 expts. with 1,2-dimethoxyethane as the solvent, a
     mixture of V and hexaphenyldisiloxane was also obtained. In the reaction of
     9,9'-bifluorene with I in Et20, heat was evolved and the mixture became
     dark. The workup gave a tarlike material from which little pure product
     could be isolated. The following results were obtained with I (olefin,
     reaction time in hrs., % yield of XI, and other products isolated given):
     1-octene, 96, 63, -; 1-octene, 48, 25, 24% Ph4Si, 22% (R3Si)20 (XII);
     1-dodecene, 72, 78, -; 1-dodecene, 48, 21, 36% R4Si, 20% XII;
     1-hexadecene, 24, 86, -; 1-octadecene, 24, 89, -; cyclohexene, 48, 87, -;
     cyclohexene, 48, 66, -; 1-methylcyclopentene, 48, 72, -;
     1,1-diphenylethylene, 2, -, 42% adduct; V, 48, 74, 70% R2C:CR2; V, 3, 52,
     74% R2C:CR2; 1,4-diphenyl-1,3-butadiene, 5, 42, 12% (R3Si)2;
     9,9'-bifluorene, 3, -, tar.
                         1960:97334 CAPLUS
ACCESSION NUMBER:
                         54:97334
DOCUMENT NUMBER:
ORIGINAL REFERENCE NO.: 54:18403e-i,18404a-c
                         Addition of silylmetallic compounds to olefins
TITLE:
AUTHOR(S):
                         Wu, T. C.; Wittenberg, Dietmar; Gilman, Henry
CORPORATE SOURCE:
                         Iowa State Univ., Ames
SOURCE:
                         Journal of Organic Chemistry (1960), 25, 596-8
                         CODEN: JOCEAH; ISSN: 0022-3263
DOCUMENT TYPE:
                         Journal
LANGUAGE:
                         Unavailable
ΙT
     18821-97-1P, Silane, triphenyl[1,2,2-triphenylethyl]-
     18834-21-4P, Silane, [2,2-diphenylethyl]triphenyl-
     RL: PREP (Preparation)
        (preparation of)
     18821-97-1 CAPLUS
RN
     Silane, triphenyl(1,2,2-triphenylethyl)- (6CI, 8CI) (CA INDEX NAME)
CN
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Ph | Ph3Si-CH-CHPh2

RN 18834-21-4 CAPLUS

CN Silane, (2,2-diphenylethyl)triphenyl- (6CI, 8CI) (CA INDEX NAME)

Ph3Si-CH2-CHPh2

L3 ANSWER 28 OF 30 CAPLUS COPYRIGHT 2008 ACS on STN

AB A series of catalytic reactions of various chlorosilanes with benzene, chlorobenzene, toluene, styrene and allylbenzene was carried out to investigate the synthesis of organosilicon compds. containing an aromatic ring. Raney Ni, AlCl3, metallic Al, H3BO3, and H2PtCl6 were tested as the catalysts. Details of expts. and yields obtained were presented in 7 tables.

ACCESSION NUMBER: 1959:94561 CAPLUS

DOCUMENT NUMBER: 53:94561
ORIGINAL REFERENCE NO.: 53:17028a-b

TITLE: Synthesis of organosilicon monomers containing an

aromatic ring

AUTHOR(S): Dolgaya, M. E.; Chernyshev, E. A.; Li, Guan-Lian CORPORATE SOURCE: Inst. Org. Chem., Acad. Sci. U.S.S.R., Moscow

SOURCE: Khim. i Prakt. Primenenie Kremneorg. Soedinenii, Trudy

Konf., Leningrad (1958), (No. 1), 99-106

DOCUMENT TYPE: Journal LANGUAGE: Unavailable

IT 18419-82-4P, Silane, trichloro[2,2-diphenylethyl]-

RL: PREP (Preparation) (preparation of) 18419-82-4 CAPLUS

CN Silane, trichloro(2,2-diphenylethyl) - (6CI, 8CI, 9CI) (CA INDEX NAME)

Ph<sub>2</sub>CH-CH<sub>2</sub>-SiCl<sub>3</sub>

RN

L3 ANSWER 29 OF 30 CAPLUS COPYRIGHT 2008 ACS on STN

AB cf. C.A. 52, 16261i. Representative members of all possible types of alkyl and aryl  $\alpha$ -silylcarbinols were treated with Na-K alloy in ether at room temperature. It was found that all these compds., with the exception of Ph3SiCH2OH (I), were readily rearranged to the isomeric silyl ether in good yield. A number of new compds. are reported. Ph3SiBz (II) with 1 equivalent MeMgI gave 85% Ph3SiCMePhOH (III), m. 120-2° (ligroine, b. 90-100°). II with excess LiAlH4 in Et2O gave 81% Ph3SiCHPhOH, m. 116-17° (ligroine). Ph3SiLi (IV) (0.0193 mole) in 50 cc. tetrahydrofuran [from 5.0 g. (Ph3Si)2 (V)] treated with 2 cc. AcH in 50 cc. tetrahydrofuran, the mixture worked up in the usual manner, and the crude product recrystd. from ligroine (b. 60-70°) and then EtOH gave 3.14 g. I, m. 101-1.5°. Ph2CH2 (42 cc.) in 150 cc. Et2O added to 172 cc. 1.45N BuLi in Et2O, refluxed 24 hrs., treated with 30.7 cc. Me3SiCl, stirred 16 hrs., poured into dilute acid, extracted with Et2O, the extract

dried and evaporated, and the residue distilled gave 29.1 g. Ph2CHSiMe3 (VI),

m.

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73-5° (EtOH). VI (14.88 g.) in 150 cc. CCl4 treated with 11.0 g.
     N-bromosuccinimide and a trace of Bz202, refluxed 16 hrs., cooled,
     filtered, the filtrate evaporated and distilled, the resulting crude
Ph2CBrSiMe3,
     b1.2 148-50°, dissolved in 150 cc. Me2CO and 25 cc. H2O, the solution
     treated with 10.4 g. AgOAc, the mixture stirred about 14 hrs. in the dark
     and filtered, the filtrate poured into 1 1. H2O and extracted with CHCl3, the
     extract dried and evaporated, and the residue recrystd. from ligroine gave
10.24
     q. Me3SiCPh2OH, m. 57.7-9.2° (ligroine). IV (from 5.0 q. V) in 50
     cc. tetrahydrofuran added dropwise with stirring at -70^{\circ} to 3.06 g.
     Ac20 in 50 cc. tetrahydrofuran, poured into dilute HCl, extracted with Et20,
and
     the residue from the extract recrystd. from CHCl3 and CHCl3-EtOH yielded 1.75
     g. MeC(OH)(SiPh3)2 (VII), m. 212-14^{\circ}, and 0.5 g. Ph3SiO(Ph3Si)CHMe
     (VIII), m. 156-7^{\circ}. PhMeCHOH (40 cc.) treated with 2.3 g. Na and
     200 cc. dry C6H6 and after 2 hrs. with 29.6 g. Ph3SiCl, refluxed 3 hrs.,
     cooled, filtered, and the residue washed with H2O left 9.0 g. (Ph3Si)2O,
     m. 218-21^{\circ}; the filtrate evaporated in vacuo and the residual oil
     distilled gave 24 cc. MePhCHOH, b1.5 63°, and 21.1 g. MePhCHOSiPh3,
     b1.0 202-4°, n20D 1.6060, m. 48-9°, also obtained, m.
     47-9^{\circ}, b1 200-4^{\circ}, n20D 1.6054, by rearrangement of III. In
     the same manner were prepared: Ph3SiOCH2Ph, 51%, m. 84.5-5.5°
     (ligroine); Ph3SiOCHMe2, 67%, m. 88-9° (iso-PrOH). Ph2CHOH (18.5
     q.) in 25 cc. C5H5N and 30 cc. dry C6H6 treated dropwise during 0.5 hr.
     with 12.8 cc. Me3SiCl, refluxed 0.5 hr., cooled, filtered, the filtrate
     poured into dilute HCl and extracted with C6H6, the C6H6 solution extracted
with acid,
     dried, evaporated, and the residue distilled yielded 18.9 g. Ph2CHOSiMe3 (IX),
     b2.0 124-4.5°, n20D 1.5265, d28 0.993. I and Ph3SiCl yielded
     similarly 20% VIII, m. 156-7°. MePh2SiCPh2OH (1.0 g.), m.
     127.5-8°, in 20 cc. dry Et20 treated with 4 drops 1:5 Na-K alloy,
     the mixture swirled, the Et2O solution decanted after 1 hr. into dilute HCl,
     dried, evaporated in vacuo, and the residue recrystd. from ligroine (b.
     60-70^{\circ}) yielded 0.86 g. Ph2CHOCH2SiPh3, m. 72-2.7^{\circ}.
     Ph3SiCMe2OH (0.8 g.), m. 155-6^{\circ}, in 30 cc. dry Et2O treated with a
     few drops Na-K alloy and the product isolated in the usual manner gave
     0.11 \text{ g. Ph}3\text{SiOH}, \text{ m. }150-1^{\circ}, \text{ and } 0.26 \text{ g. Ph}3\text{SiOCHMe}2, \text{ m.}
     88-9°. Similarly, Ph3SiCPh2OH (X), m. 156-9°, gave during 3
     min. 95% Ph3SiOCHPh2, m. 83-4°. Ph3SiCMePhOH, m. 120-2°,
     gave during 18 hrs. 67% Ph3SiOCHMePh, m. 48-9°; Ph3SiCHPhOH (XI),
     m. 116-17°, gave during 1 hr. 65% Ph3SiOCH2Ph, m. 84.5-5.5°;
     Ph3SiCHMeOH, m. 101-1.5°, gave during 4.5 hrs. 67% Ph3SiOCH2Me, m.
     64\text{--}5^{\circ}.~\text{IX, m. }57.7\text{--}9.2^{\circ}\text{, gave during }1.5~\text{hrs. }60\%
     Me3SiOCHPh2, b1 116°, b2 124-4.5°, n20D 1.5265, d28 0.993.
     VII, m. 212-14^{\circ}, in 1:3 C6H6-Et2O gave in the same manner during
     143 hrs. 82% VIII, m. 156-7.5°. VII (1.0 g.) in 40 cc.
     tetrahydrofuran treated during 20 hrs. with a few drops Na-K alloy gave
     1.0 g. gummy solid which recrystd. from ligroine (b. 90-100°) gave
     0.3 g. Ph3SiOH, m. 148-50^\circ, and 0.12 g. unidentified white solid, m. 210-14^\circ. XI (0.20 g.), 20 cc. Me2CO, 20 cc. C6H6, and 0.22 g.
     (iso-PrO)3Al refluxed 24 hrs. and worked up in the usual manner yielded
     0.19 g. (crude) Ph3SiOCH2Ph, m. 81-3°. Ph2CHOSiPh3 (1.5 g.)
     treated during 16 hrs. with 0.5 cc. Na-K alloy in 25 cc. Et20 and the
     mixture worked up in the usual manner gave 0.64 g. Ph3SiOH, m.
     151-2^{\circ}. X (0.5 g.) in 10 cc. CCl4 treated during 10 min. with a
     few drops Na-K alloy in the usual manner yielded only 0.42 g. unchanged X,
     m. 155-7°.
ACCESSION NUMBER:
                          1959:94560 CAPLUS
                          53:94560
DOCUMENT NUMBER:
```

Isomerization of some  $\alpha$ -hydroxysilanes to silyl

ORIGINAL REFERENCE NO.: 53:17027a-i,17028a

TITLE:

ethers. II

AUTHOR(S): Brook, A. G.; Warner, C. M.; McGriskin, Mary E.

CORPORATE SOURCE: Univ. of Toronto, Can.

SOURCE: Journal of the American Chemical Society (1959), 81,

981 - 3

CODEN: JACSAT; ISSN: 0002-7863

DOCUMENT TYPE: Journal LANGUAGE: Unavailable

IT 18419-82-4P, Silane, trichloro[2,2-diphenylethyl]-

RL: PREP (Preparation)
(preparation of)
18419-82-4 CAPLUS

CN Silane, trichloro(2,2-diphenylethyl) - (6CI, 8CI, 9CI) (CA INDEX NAME)

Ph<sub>2</sub>CH-CH<sub>2</sub>-SiCl<sub>3</sub>

RN

L3 ANSWER 30 OF 30 CAPLUS COPYRIGHT 2008 ACS on STN

AB cf. C.A. 52, 7187b. Refluxing 130 g. C12CHSiC13, 224 g. PhC1, and 10 g. AlC13 64 hrs., followed by addition of 20 q. POC13 to separate the catalyst as POC13.AlC13, gave on distillation of the filtrate 48 g. unreacted starting material and 49.5% (C1C6H4)2CHSiCl3, b8 197-8°, n20D 1.5945, d20 1.4343. Similarly C12CHSiMeC12 and C6H6 gave 5.6% Ph2CHSiMeC12, b3 134-5°, 1.5735, 1.1917. PhCl gave 42.3% (ClC6H4)2CHSiMeCl2, b4.5 196-7°, 1.5908, 1.3383, MePh gave 4.1% (MeC6H4)2CHSiMeCl2, b4 159-63°, 1.5639, 1.1392. MeCCl2SiCl3 and C6H6 gave 38% MeCPh2SiCl3, b15 173°, 1.5845, 1.3111. PhCl gave 8.7% C1C6H4CHMeSiCl3, b3 126-8°, 1.5392, 1.3528, and 40% (C1C6H4)2CMeSiCl3, b5 226-7°, 1.5985, 1.4125. MePh gave 41% MeC6H4CHMeSiCl3, b3 96-8°, 1.5222, 1.2271, and 5.2% (MeC6H4)2CMeSiCl3, b3 156-60°, 1.5760, 1.2221. Cl2CHCH2SiCl3 and C6H6 gave 15% Ph2CHCH2SiCl3, b6.5 168-9°, m. 67-8°. The use of PhCl resulted in 25.8% (ClC6H4)2CHCH2SiCl3, b6 198-200°, 1.5830, 1.3954, while the use of MePh gave 10.7% MeC6H4CH2CH2SiCl3, b3  $105-6^{\circ}$ , 1.5178, 1.2139, and 3.1% (MeC6H4)2CHCH2SiCl3, b5 173-4°, m. 53-4°. Reaction of C1CH2CHClSiCl3 with C6H6 gave 4.2% PhCH2CH2SiCl3, b5 98-9°, 1.5180, 1.2394, and 9.5% PhCH2CHPhSiCl3, b5 162-3°, m. 60-1°. Similarly, PhCl gave 4.9% C1C6H4CH2CH2SiCl3, b5 122°, 1.5312, 1.3459, and 27.4% ClC6H4CH2CH(C6H4Cl)SiCl3, b5 207-8°, 1.5833, 1.3971, while MePh gave 19.6% MeC6H4CH2CH2SiCl3, b7 113-4.5°, 1.5178, 1.2125, and 5.6% MeC6H4CH2CH(C6H4Me)SiCl3, b7 173.5-5°, 1.5590, 1.2061. Treatment of appropriate chlorides with MeMgCl gave the following silanes: MeC6H4CHMeSiMe3, b6 88-9°, 1.4955, 0.8756; MeC6H4CH2CH2SiMe3, b745 222-4°, 1.4882, 0.8640. MeC6H4CH2CH2SiMe3 (from other sources), b742 223-4°, 1.4878, 0.8637. The ultraviolet absorption spectra of the products are shown and indicate the predominance of p-isomers among the products listed above.

ACCESSION NUMBER: 1958:97653 CAPLUS

DOCUMENT NUMBER: 52:97653 ORIGINAL REFERENCE NO.: 52:17150b-f

TITLE: Silicoalkylation of aromatic compounds by

dichloroalkylsilane chlorides

AUTHOR(S): Chernyshev, E. A.; Dolgaya, M. E.; Egorov, Yu. P.;

Semenov, L. V.; Petrov, A. D.

CORPORATE SOURCE: Inst. Org. Chem., Acad. Sci. U.S.S.R., Moscow SOURCE: Zhurnal Obshchei Khimii (1958), 28, 613-16

CODEN: ZOKHA4; ISSN: 0044-460X

DOCUMENT TYPE: Journal LANGUAGE: Unavailable

```
18419-82-4P, Silane, trichloro[2,2-diphenylethyl]-
ΤТ
     RL: PREP (Preparation)
        (preparation of)
RN
     18419-82-4 CAPLUS
     Silane, trichloro(2,2-diphenylethyl) - (6CI, 8CI, 9CI) (CA INDEX NAME)
CN
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                  IMSPRODUCT reloaded with enhancements
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                  WPINDEX/WPIDS/WPIX enhanced with ECLA and current
                  U.S. National Patent Classification
                  IFICDB, IFIPAT, and IFIUDB enhanced with new custom
NEWS 14 MAR 31
                  IPC display formats
 NEWS 15 MAR 31
                  CAS REGISTRY enhanced with additional experimental
                  spectra
 NEWS 16 MAR 31
                  CA/CAplus and CASREACT patent number format for U.S.
                  applications updated
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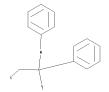
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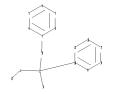
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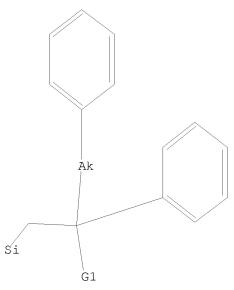
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1  2 16 17 18
ring nodes :
3  4  5  6  7  8  9  10  11  12  13  14
chain bonds :
1-2 1-17 2-16 2-18 2-10 3-18
ring bonds :
3-4 3-8 4-5 5-6 6-7 7-8 9-10 9-14 10-11 11-12 12-13 13-14
exact/norm bonds :
2-16 2-18 3-18
exact bonds :
1-2 1-17 2-10
normalized bonds :
3-4 3-8 4-5 5-6 6-7 7-8 9-10 9-14 10-11 11-12 12-13 13-14
```

G1:CH3,H

Match level:
1:CLASS 2:CLASS 3:Atom 4:Atom 5:Atom 6:Atom 7:Atom 8:Atom 9:Atom 10:Atom 11:Atom 12:Atom 13:Atom 14:Atom 16:CLASS 17:CLASS 18:CLASS

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G1 Me, H

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L3 41 L2

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L3 ANSWER 1 OF 41 CAPLUS COPYRIGHT 2008 ACS on STN

An ew hydrosilylative cross-coupling reaction of a variety of alkynes with several alkenes, which is catalyzed by a cationic palladium complex, [Pd(η3-C3H5)(cod)]+[PF6]- (A, 1 mol %) without or with added PPh3 ligand, was studied systematically. The reaction using HSiCl3 as an addend afforded more or less two types of products consisting of four possible derivs., CH:CR2CHR3CHR4SiCl3, which always contained 4-trichlorosilyl-1-butene frameworks, in acceptable combined yields. The coupling pattern was dependent both on the precatalyst A in the absence or presence of PPh3 [also P(C6F5)3] and on the combination of the alkyne and alkene counterpart employed. A possible catalytic cycle that involves an initial hydropalladation of an alkyne, followed by a facile and specific carbopalladation of an alkene, is proposed. At the same time, the lack of regioselectivity in the latter step is noted. The effect of the added phosphine ligand on the coupling pattern is briefly discussed.

ACCESSION NUMBER: 2007:1124227 CAPLUS

DOCUMENT NUMBER: 148:11284

TITLE: Cationic palladium complex-catalyzed hydrosilylative

cross-coupling of alkynes with alkenes. 1,4-addition of trichlorosilane to form 4-silyl-1-butene framework

AUTHOR(S): Shimamoto, Takamitsu; Chimori, Motoharu; Sogawa,

Hiroaki; Harada, Yuki; Aoki, Masaharu; Yamamoto, Keiji

CORPORATE SOURCE: Department of Materials Science and Environmental

Engineering Tokyo University of Science Yamaguchi

Engineering, Tokyo University of Science, Yamaguchi, 1-1-1 Daigaku-Dori, Sanyo-Onoda, Yamaguchi, 756-0884,

Japan

SOURCE: Bulletin of the Chemical Society of Japan (2007),

80(9), 1814-1823

CODEN: BCSJA8; ISSN: 0009-2673

PUBLISHER: Chemical Society of Japan

DOCUMENT TYPE: Journal LANGUAGE: English

OTHER SOURCE(S): CASREACT 148:11284

IT 872555-19-6P 872555-23-2P

RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT

(Reactant or reagent)

(preparation of silylbutene framework via cationic palladium complex-catalyzed hydrosilylative cross-coupling of alkynes with alkenes in presence of trichlorosilane)

RN 872555-19-6 CAPLUS

CN Benzene, 1,1'-[1-methylene-2-[(trichlorosily1)methyl]-1,2-ethanediyl]bis-(CA INDEX NAME)

$$\begin{array}{c|c} ^{\rm H2C} & {\rm Ph} \\ & | & | \\ {\rm Ph-C-CH-CH_2-SiCl_3} \end{array}$$

RN 872555-23-2 CAPLUS

CN Benzene, 1,1'-[(1E)-3-[(trichlorosily1)methy1]-1-propene-1,3-diy1]bis-(CA INDEX NAME)

Double bond geometry as shown.

IT 872555-34-5P 872555-36-7P

RL: SPN (Synthetic preparation); PREP (Preparation) (preparation of silylbutene framework via cationic palladium complex-catalyzed hydrosilylative cross-coupling of alkynes with alkenes in presence of trichlorosilane)

RN 872555-34-5 CAPLUS

CN Benzene, 1,1'-[1-methylene-2-[(triethoxysily1)methyl]-1,2-ethanediyl]bis-(CA INDEX NAME)

RN 872555-36-7 CAPLUS

CN Benzene, 1,1'-[(1E)-3-[(triethoxysilyl)methyl]-1-propene-1,3-diyl]bis-(CA INDEX NAME)

Double bond geometry as shown.

REFERENCE COUNT: 55 THERE ARE 55 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L3 ANSWER 2 OF 41 CAPLUS COPYRIGHT 2008 ACS on STN

AB  $\beta$ -(Alkenyl)ethylalkoxysilanes are prepared by cross-coupling reaction of alkynes with alkenes in the presence of [( $\eta$ 3-C3H5)PdA]+PF6- (A = 1,5-cyclooctadiene, aromatic isocyanide, N-heterocyclic carbene) and optional PPh3, treatment with chlorohydrosilanes, and substitution of the resulting  $\beta$ -(alkenyl)ethylchlorosilanes with alcs. Thus, PHC.tplbond.CH was treated with 1-hexene in the presence of [( $\eta$ 3-C3H5)Pd(cod)]+PF6- [cod = 1,5-cyclooctadiene; prepared from [( $\eta$ 3-C3H5)Pd]2C12, 1,5-cyclooctadiene, and AgPF6] and treated with HSiCl3 to give 60/40 CH2:CPhCH(C4H9)CH2SiCl3/CH2:CPhCH2CH(C4H9)SiCl3 mixture, which was substituted with EtOH.

ACCESSION NUMBER: 2007:323594 CAPLUS

DOCUMENT NUMBER: 146:358976

TITLE: Preparation of  $\beta$ -(alkenyl)ethylalkoxysilanes from

alkynes, alkenes, and chlorohydrosilanes via

 $\beta$ -(alkenyl)ethylchlorosilanes

INVENTOR(S):
Yamamoto, Kyoji

PATENT ASSIGNEE(S): Tokyo University of Science, Japan

SOURCE: Jpn. Kokai Tokkyo Koho, 23pp.

CODEN: JKXXAF

DOCUMENT TYPE: Patent

LANGUAGE: Japanese

FAMILY ACC. NUM. COUNT:

PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 2007070237	A	20070322	JP 2005-255983	20050905
PRIORITY APPLN. INFO.:			JP 2005-255983	20050905
OTHER SOURCE(S):	CASREA	ACT 146:3589	76; MARPAT 146:358976	

OTHER SOURCE(S):

872555-19-6P

RL: IMF (Industrial manufacture); RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent) (preparation of  $\beta$ -(alkenyl)ethylalkoxysilanes by cross-coupling of alkynes with alkenes in the presence of Pd complex catalysts, substitution with chlorohydrosilanes, and substitution with alcs.)

RN 872555-19-6 CAPLUS

Benzene, 1,1'-[1-methylene-2-[(trichlorosily1)methyl]-1,2-ethanediy1]bis-CN (CA INDEX NAME)

$$\begin{array}{c|c} {\rm H_2C} & {\rm Ph} \\ & | & | \\ {\rm Ph-C-CH-CH_2-SiCl_3} \end{array}$$

ANSWER 3 OF 41 CAPLUS COPYRIGHT 2008 ACS on STN T.3 GΙ

AB The 1-menthone-derived TADDOL phosphite I catalyzes highly enantioselective conjugate addns. of acyl silanes to  $\alpha, \beta$ unsatd. amides. P-Methoxybenzoylcyclohexyldimethylsilane adds to a variety of N,N-dimethylacrylamides in the presence of the lithium salt of I. In many instances the  $\alpha$ -silyl- $\gamma$ -keto amide product undergoes facile enantioenrichment (to 97-99% ee) upon recrystn. Desilylation with  ${\tt HF} \cdot {\tt pyr}$  affords the formal Stetter addition products. Baeyer-Villiger oxidation of the desilylated  $\gamma$ -keto amides affords useful ester products. An X-ray diffraction study of I reveals that the iso-Pr group of the menthone ketal influences the position of the syn-pseudoaxial Ph group in the TADDOL structure. Through a crossover experiment, the silicon migration step in the reaction mechanism is shown to be strictly intramol.

ACCESSION NUMBER: 2006:122067 CAPLUS

144:369738 DOCUMENT NUMBER:

TITLE: Metallophosphite-Catalyzed Asymmetric Acylation of

 $\alpha$ ,  $\beta$ -Unsaturated Amides

AUTHOR(S): Nahm, Mary R.; Potnick, Justin R.; White, Peter S.;

Johnson, Jeffrey S.

CORPORATE SOURCE: Department of Chemistry, University of North Carolina,

Chapel Hill, NC, 27599-3290, USA

SOURCE: Journal of the American Chemical Society (2006),

128(8), 2751-2756

CODEN: JACSAT; ISSN: 0002-7863

PUBLISHER: American Chemical Society

DOCUMENT TYPE: Journal LANGUAGE: English

OTHER SOURCE(S): CASREACT 144:369738
IT 881883-38-1P 881883-39-2P 881883-65-4P
881883-67-6P 881883-68-7P 881883-69-8P

881883-70-1P 881883-71-2P

RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)

(metallophosphite-catalyzed asym. acylation of  $\alpha,\beta\text{-unsatd.}$  amides with acylsilanes)

RN 881883-38-1 CAPLUS

CN Benzenebutanamide,  $\alpha$ -(dimethylphenylsilyl)-N,N-dimethyl- $\gamma$ -oxo- $\beta$ -phenyl-, ( $\alpha$ R, $\beta$ R)-rel- (9CI) (CA INDEX NAME)

Relative stereochemistry.

RN 881883-39-2 CAPLUS

CN Benzenebutanamide,  $\alpha$ -(cyclohexyldimethylsilyl)-4-methoxy-N,N-dimethyl- $\gamma$ -oxo- $\beta$ -phenyl-, ( $\alpha$ R, $\beta$ R)-rel- (9CI) (CA INDEX NAME)

Relative stereochemistry.

RN 881883-65-4 CAPLUS

CN Benzenebutanamide,  $\alpha$ -(cyclohexyldimethylsilyl)-4-methoxy- $\beta$ -(4-methoxyphenyl)-N,N-dimethyl- $\gamma$ -oxo-, ( $\alpha$ R, $\beta$ R)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.

RN 881883-67-6 CAPLUS

CN Benzenebutanamide,  $\alpha$ -(cyclohexyldimethylsilyl)-4-methoxy-N,N-dimethyl- $\beta$ -(4-methylphenyl)- $\gamma$ -oxo-, ( $\alpha$ R, $\beta$ R)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.

RN 881883-68-7 CAPLUS

CN Benzenebutanamide,  $\alpha$ -(cyclohexyldimethylsilyl)-4-methoxy-N,N-dimethyl- $\beta$ -(3-methylphenyl)- $\gamma$ -oxo-, ( $\alpha$ R, $\beta$ R)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.

RN 881883-69-8 CAPLUS

CN Benzenebutanamide,  $\beta$ -(4-chlorophenyl)- $\alpha$ -(cyclohexyldimethylsilyl)-4-methoxy-N,N-dimethyl- $\gamma$ -oxo-, ( $\alpha$ R, $\beta$ R)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.

RN 881883-70-1 CAPLUS

CN Benzenebutanamide,  $\alpha$ -(cyclohexyldimethylsilyl)-4-methoxy-N,N-dimethyl- $\gamma$ -oxo- $\beta$ -[4-(trifluoromethyl)phenyl]-, ( $\alpha$ R, $\beta$ R)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.

RN 881883-71-2 CAPLUS

CN 2-Naphthalenepropanamide,  $\alpha$ -(cyclohexyldimethylsilyl)- $\beta$ -(4-methoxybenzoyl)-N,N-dimethyl-,  $(\alpha R, \beta R)$ - (CA INDEX NAME)

Absolute stereochemistry.

IT 905948-10-9P

RL: SPN (Synthetic preparation); PREP (Preparation) (metallophosphite-catalyzed asym. acylation of  $\alpha,\beta$ -unsatd.

amides with acylsilanes)

RN 905948-10-9 CAPLUS

CN Benzenebutanamide, N,N-dimethyl- $\gamma$ -oxo- $\beta$ -phenyl- $\alpha$ - (triethylsilyl)-, ( $\alpha$ R, $\beta$ R)-rel- (9CI) (CA INDEX NAME)

Relative stereochemistry.

REFERENCE COUNT: 36 THERE ARE 36 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L3 ANSWER 4 OF 41 CAPLUS COPYRIGHT 2008 ACS on STN

AB A cationic palladium complex-catalyzed cross-coupling of alkynes with alkenes is presented, which occurs selectively under the hydrosilylation conditions using trichlorosilane. The unique reaction might be well understood in terms of an initial hydropalladation of a given 1-alkyne to form regioselectively a 1-alkenylpalladium species, which, in turn, undergoes easily and specifically an alkene insertion. The resulting homoallylic organopalladium species terminates one catalytic cycle by substituting the palladium center with a trichlorosilyl group to give product(s).

ACCESSION NUMBER: 2005:1184881 CAPLUS

DOCUMENT NUMBER: 144:88343

TITLE: Cationic Palladium-Catalyzed Hydrosilylative

Cross-Coupling of Alkynes with Alkenes

AUTHOR(S): Shimamoto, Takamitsu; Chimori, Motoharu; Sogawa,

Hiroaki; Yamamoto, Keiji

CORPORATE SOURCE: Department of Materials Science and Environmental

Engineering, Tokyo University of Science, Yamaguchi 1-1-1 Daigaku-Dori, Sanyo-Onoda, Yamaguchi, 756-0884,

Japan

SOURCE: Journal of the American Chemical Society (2005),

127(47), 16410-16411

CODEN: JACSAT; ISSN: 0002-7863

PUBLISHER: American Chemical Society

DOCUMENT TYPE: Journal LANGUAGE: English

OTHER SOURCE(S): CASREACT 144:88343

IT 872555-19-6P 872555-23-2P

RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT

(Reactant or reagent)

(cationic palladium-catalyzed hydrosilylative cross-coupling of alkynes with alkenes)

RN 872555-19-6 CAPLUS

CN Benzene, 1,1'-[1-methylene-2-[(trichlorosily1)methyl]-1,2-ethanediyl]bis-(CA INDEX NAME)

$$\begin{array}{c|c} ^{\rm H2C} & {\rm Ph} \\ & | & | \\ {\rm Ph-C-CH-CH_2-SiCl_3} \end{array}$$

RN 872555-23-2 CAPLUS

CN Benzene, 1,1'-[(1E)-3-[(trichlorosily1)methy1]-1-propene-1,3-diy1]bis-

(CA INDEX NAME)

Double bond geometry as shown.

IT 872555-34-5P 872555-36-7P

RL: SPN (Synthetic preparation); PREP (Preparation) (cationic palladium-catalyzed hydrosilylative cross-coupling of alkynes with alkenes)

RN 872555-34-5 CAPLUS

CN Benzene, 1,1'-[1-methylene-2-[(triethoxysily1)methyl]-1,2-ethanediyl]bis-(CA INDEX NAME)

RN 872555-36-7 CAPLUS

CN Benzene, 1,1'-[(1E)-3-[(triethoxysilyl)methyl]-1-propene-1,3-diyl]bis-(CA INDEX NAME)

Double bond geometry as shown.

REFERENCE COUNT: 29 THERE ARE 29 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L3 ANSWER 5 OF 41 CAPLUS COPYRIGHT 2008 ACS on STN

AB 3-Methoxyacylsilanes undergo stereoselective addition of organometallic nucleophiles, affording 1,3-syn- and 1,3-anti-3-methoxy-1- hydroxyalkylsilanes, which were converted to the corresponding 1,3-diol ethers by protiodesilylation. Reaction of RCH(OMe)CH2COSiMe3 with R1M (M = Li, MgBr, AlMe2, CeCl2) gave RCH(OMe)CH2CR1(OH)SiMe3 (R = Ph, Me, n-Pr, iPr); organolithium reagents gave predominantly 1,3-anti-diastereomers, whereas methylcerium and trialkylaluminum gave the 1,3-syn-isomers. Addition of MeLi to 2,3-anti-RCH(OMe)CHPhCOSiMe3 gave 1,2-syn-RCH(OMe)CHPhCMe(OH)SiMe3 (5a,b, R = Ph, Me) trimethylaluminum gave rise to 1,2-anti-RCH(OMe)CHPhCMe(OH)SiMe3 (4a,b; same R). The stereoselectivity of 1,3-asym. induction in the nucleophilic addition to  $\beta$ - methoxyacylsilanes is largely dependent on the kind of nucleophiles. The protiodesilylation of the resulting  $\alpha$ -silylalcs. proceeds with complete retention of the configuration.

ACCESSION NUMBER: 2005:1160096 CAPLUS

DOCUMENT NUMBER: 144:36393

TITLE: Stereoselective construction of 1,3-diol derivatives via nucleophilic reaction to  $\beta$ -methoxyacylsilanes

AUTHOR(S): Honda, Mitsunori; Mikami, Yoshimi; Sanjyo, Takeshi;

Segi, Masahito; Nakajima, Tadashi

CORPORATE SOURCE: Division of Material Sciences, Graduate School of

Natural Science and Technology, Kanazawa University,

Kakuma-machi, Kanazawa, 920-1192, Japan Chemistry Letters (2005), 34(10), 1432-1433

CODEN: CMLTAG; ISSN: 0366-7022

PUBLISHER: Chemical Society of Japan

DOCUMENT TYPE: Journal LANGUAGE: English

OTHER SOURCE(S): CASREACT 144:36393

IT 482662-09-9 626235-41-4

SOURCE:

RL: RCT (Reactant); RACT (Reactant or reagent)

(preparation of syn- and anti-isomers of 1-silyl 3-methoxy-1-alkanols by stereoselective nucleophilic addition of lithium, aluminum and cerium organometallic compds. to acylsilanes)

RN 482662-09-9 CAPLUS

CN Silane, [(2R,3S)-3-methoxy-1-oxo-2,3-diphenylpropyl]trimethyl-, rel- (9CI) (CA INDEX NAME)

Relative stereochemistry.

RN 626235-41-4 CAPLUS

CN Silane, [(2R,3R)-3-methoxy-1-oxo-2,3-diphenylpropyl]trimethyl-, rel- (9CI) (CA INDEX NAME)

Relative stereochemistry.

IT 626235-47-0P 626235-48-1P 870699-88-0P

RL: SPN (Synthetic preparation); PREP (Preparation) (preparation of syn- and anti-isomers of 1-silyl 3-methoxy-1-alkanols by stereoselective nucleophilic addition of lithium, aluminum and cerium organometallic compds. to acylsilanes)

RN 626235-47-0 CAPLUS

CN Benzenepropanol,  $\gamma$ -methoxy- $\alpha$ -methyl- $\beta$ -phenyl- $\alpha$ - (trimethylsilyl)-, ( $\alpha$ R,  $\beta$ R,  $\gamma$ R)-rel- (CA INDEX NAME)

Relative stereochemistry.

RN 626235-48-1 CAPLUS

Benzenepropanol,  $\gamma$ -methoxy- $\alpha$ -methyl- $\beta$ -phenyl- $\alpha$ -CM(trimethylsilyl)-,  $(\alpha R, \beta R, \gamma S)$ -rel- (CA INDEX NAME)

Relative stereochemistry.

RN 870699-88-0 CAPLUS

CN Benzenepropanol,  $\gamma$ -methoxy- $\alpha$ -methyl- $\beta$ -phenyl- $\alpha$ -(trimethylsilyl)-,  $(\alpha R, \beta S, \gamma R)$ -rel- (CA INDEX NAME)

Relative stereochemistry.

REFERENCE COUNT: 21 THERE ARE 21 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L3 ANSWER 6 OF 41 CAPLUS COPYRIGHT 2008 ACS on STN

A reference to Reich et al. is added. Reference [10] should read as "(a) H. J. AΒ Reich, R. C. Holtan, C. Bolm, J. Am. Chemical Society 1990, 112, 5609-5617; (b)

K. Takeda, T. Tanaka, Synlett 1999, 705-708.".

ACCESSION NUMBER: 2005:780897 CAPLUS

DOCUMENT NUMBER: 143:386980

TITLE: Metallophosphite-induced nucleophilic acylation of

 $\alpha, \beta$ -unsaturated amides: Facilitated

catalysis by a diastereoselective retro [1,4] Brook

rearrangement. [Erratum to document cited in

CA143:0781421

AUTHOR(S): Nahm, Mary R.; Xin, Linghu; Potnick, Justin R.; Yates,

Christopher M.; White, Peter S.; Johnson, Jeffrey S.

CORPORATE SOURCE: Department of Chemistry, University of North Carolina,

Chapel Hill, Chapel Hill, NC, 27599-3290, USA

Angewandte Chemie, International Edition (2005), SOURCE:

44(30), 4660

CODEN: ACIEF5; ISSN: 1433-7851

Wiley-VCH Verlag GmbH & Co. KGaA PUBLISHER:

DOCUMENT TYPE: Journal LANGUAGE: English

ΙT 855333-38-9P

> RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)

(preparation of  $\alpha$ -silyl  $\gamma$ -keto amide derivs. via stereoselective

conjugate addition using benzoyl silanes (aldehyde surrogates) and Michael

acceptors as reactants and 1,3-dioxolo[4,5-e][1,3,2]dioxaphosphepin

oxide derivative (phosphite) as catalyst)

RN 855333-38-9 CAPLUS

CN 1,4-Butanedione, 2-(dimethylphenylsilyl)-1-(4-morpholinyl)-3,4-diphenyl-, (2R, 3R) - (CA INDEX NAME)

Absolute stereochemistry.

IT 855333-20-9P 855333-21-0P 855333-22-1P

RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)

(preparation of  $\alpha$ -silyl  $\gamma$ -keto amide derivs, via stereoselective conjugate addition using benzoyl silanes (aldehyde surrogates) and Michael acceptors as reactants and phosphite derivative as catalyst (Erratum))

RN 855333-20-9 CAPLUS

CN 1,4-Butanedione, 2-(dimethylphenylsilyl)-1-(4-morpholinyl)-3,4-diphenyl-, (2R,3R)-rel- (CA INDEX NAME)

Relative stereochemistry.

RN 855333-21-0 CAPLUS

CN 1,4-Butanedione, 2-(dimethylphenylsilyl)-3-(4-methoxyphenyl)-1-(4-morpholinyl)-4-phenyl-, (2R,3R)-rel- (CA INDEX NAME)

Relative stereochemistry.

RN 855333-22-1 CAPLUS

CN 1,4-Butanedione, 2-(4-chlorophenyl)-3-(dimethylphenylsilyl)-4-(4-morpholinyl)-1-phenyl-, (2R,3R)-rel- (CA INDEX NAME)

Relative stereochemistry.

L3 ANSWER 7 OF 41 CAPLUS COPYRIGHT 2008 ACS on STN

AB Intermol. alkene acylation reactions between acyl silanes and  $\alpha,\beta\text{-unsatd.}$  amides with metallo phosphite catalysis afford  $\alpha\text{-silyl}\ \gamma\text{-keto}$  amide derivs. With high diastereoselectivity. These can be converted into the corresponding  $\gamma\text{-keto}$  amide derivs. and  $\alpha\text{-bromo}\ \gamma\text{-keto}$  amide derivs. Asym. catalysis of the

acylation delivers the  $\gamma$ -keto amide in the highest

acylation delivers the f keto and e in the highest

enantioselectivity yet reported for an intermol. Stetter-type reaction.

ACCESSION NUMBER: 2005:390712 CAPLUS

DOCUMENT NUMBER: 143:78142

TITLE: Metallophosphite-induced nucleophilic acylation of

 $\alpha$ ,  $\beta$ -unsaturated amides: Facilitated

catalysis by a diastereoselective retro [1,4] Brook

rearrangement

AUTHOR(S): Nahm, Mary R.; Xin, Linghu; Potnick, Justin R.; Yates,

Christopher M.; White, Peter S.; Johnson, Jeffrey S.

CORPORATE SOURCE: Department of Chemistry, University of North Carolina,

Chapel Hill, Chapel Hill, NC, 27599-3290, USA

SOURCE: Angewandte Chemie, International Edition (2005),

44(16), 2377-2379

CODEN: ACIEF5; ISSN: 1433-7851

PUBLISHER: Wiley-VCH Verlag GmbH & Co. KGaA

DOCUMENT TYPE: Journal LANGUAGE: English

OTHER SOURCE(S): CASREACT 143:78142

IT 855333-38-9P

RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)

(preparation of  $\alpha$ -silyl  $\gamma$ -keto amide derivs. via stereoselective conjugate addition using benzoyl silanes (aldehyde surrogates) and Michael

acceptors as reactants and 1,3-dioxolo[4,5-e][1,3,2]dioxaphosphepin

oxide derivative (phosphite) as catalyst)

RN 855333-38-9 CAPLUS

CN 1,4-Butanedione, 2-(dimethylphenylsilyl)-1-(4-morpholinyl)-3,4-diphenyl-, (2R,3R)- (CA INDEX NAME)

Absolute stereochemistry.

RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)

(preparation of  $\alpha$ -silyl  $\gamma$ -keto amide derivs. via stereoselective conjugate addition using benzoyl silanes (aldehyde surrogates) and Michael acceptors as reactants and phosphite derivative as catalyst)

RN 855333-20-9 CAPLUS

CN 1,4-Butanedione, 2-(dimethylphenylsilyl)-1-(4-morpholinyl)-3,4-diphenyl-, (2R,3R)-rel- (CA INDEX NAME)

Relative stereochemistry.

RN 855333-21-0 CAPLUS

CN 1,4-Butanedione, 2-(dimethylphenylsilyl)-3-(4-methoxyphenyl)-1-(4-morpholinyl)-4-phenyl-, (2R,3R)-rel- (CA INDEX NAME)

Relative stereochemistry.

RN 855333-22-1 CAPLUS

CN 1,4-Butanedione, 2-(4-chlorophenyl)-3-(dimethylphenylsilyl)-4-(4-morpholinyl)-1-phenyl-, (2R,3R)-rel- (CA INDEX NAME)

Relative stereochemistry.

REFERENCE COUNT:

33 THERE ARE 33 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L3 ANSWER 8 OF 41 CAPLUS COPYRIGHT 2008 ACS on STN

AB The reaction of C,O,O-tris(trimethylsilyl)ketene acetal 1 with saturated, cyclic and aromatic ketones 2 (e.g., CH3C(O)Ph) proceeds smoothly in the presence of TiCl4 to give (E)- $\alpha$ , $\beta$ -unsatd. carboxylic acids 3

(e.g., (E)-PhCMe:CHCO2H) with fairly good stereoselectivity. With

 $\alpha$ ,  $\beta$ -unsatd. ketones 4 (e.g., CH3C(O)CH:CHPh),

 $\alpha$ -trimethylsilyl  $\delta$ -ketoacids 5 [syn + anti; e.g.,

CH3C(O)CH2CHPhCH(SiMe3)CO2H] were obtained according to Michael-type 1,4

addition These diastereoisomers are separated and the configurations of 5a are

achieved by x-ray mol. anal.

ACCESSION NUMBER: 2005:358698 CAPLUS

DOCUMENT NUMBER: 143:60027

TITLE: Two-carbon homologation of ketones via silyl ketene

acetals: synthesis of  $\alpha$ ,  $\beta$ -unsaturated acids

and  $\alpha$ -trimethylsilyl  $\delta$ -ketoacids

AUTHOR(S): Bellassoued, Moncef; Mouelhi, Sinda; Fromentin,

Pierre; Gonzalez, Aurelien

CORPORATE SOURCE: Laboratoire de Synthese Organometallique, Universite

de Cergy-Pontoise, Cergy-Pontoise, 95031, Fr.

SOURCE: Journal of Organometallic Chemistry (2005), 690(9),

2172-2179

CODEN: JORCAI; ISSN: 0022-328X

PUBLISHER: Elsevier B.V.

DOCUMENT TYPE: Journal LANGUAGE: English

OTHER SOURCE(S): CASREACT 143:60027

IT 854198-42-8P 854198-56-4P

RL: SPN (Synthetic preparation); PREP (Preparation)

(stereoselective reaction of tris(trimethylsilyl)ketene acetal with unsatd. ketones in presence of titanium chloride to give silylated

ketoacids)

RN 854198-42-8 CAPLUS

CN Benzenepropanoic acid,  $\beta$ -(2-oxo-2-phenylethyl)- $\alpha$ -(trimethylsilyl)-, ( $\alpha$ R, $\beta$ S)-rel- (CA INDEX NAME)

Relative stereochemistry.

RN 854198-56-4 CAPLUS

CN Benzenepropanoic acid,  $\beta$ -(2-oxo-2-phenylethyl)- $\alpha$ -(trimethylsilyl)-, ( $\alpha$ R,  $\beta$ R)-rel- (CA INDEX NAME)

Relative stereochemistry.

REFERENCE COUNT: 15 THERE ARE 15 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L3 ANSWER 9 OF 41 CAPLUS COPYRIGHT 2008 ACS on STN

AB The treatment of acetyltrimethylsilane with LDA, followed by reaction of the resulting enolate with the excess amount of aldehydes gave the corresponding 1,3-diol derivs. in moderate yields with perfect

diastereoselectivity as a single regioisomer via tandem aldol-Tishchenko reaction, whereas the reaction with  $\alpha-$  branched aldehydes under similar conditions gives a mixture of two regioisomers. The reaction using benzyl trimethylsilyl ketone afforded the corresponding 1,3-diol monoesters having three contiguous stereogenic centers with perfect levels of stereochem. control in 1-pot.

ACCESSION NUMBER: 2005:351230 CAPLUS

DOCUMENT NUMBER: 143:43919

TITLE: Stereoselective tandem aldol-tishchenko reaction with

acylsilanes

AUTHOR(S): Honda, Mitsunori; Iwamoto, Ryota; Nogami, Yoshie;

Segi, Masahito

CORPORATE SOURCE: Division of Material Sciences, Graduate School of

Natural Science and Technology, Kanazawa University,

Kanazawa, 920-1192, Japan

SOURCE: Chemistry Letters (2005), 34(4), 466-467

CODEN: CMLTAG; ISSN: 0366-7022

PUBLISHER: Chemical Society of Japan

DOCUMENT TYPE: Journal LANGUAGE: English

OTHER SOURCE(S): CASREACT 143:43919

IT 853601-60-2P 853601-69-1P

RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)

(stereoselective tandem aldol-tishchenko reaction of aldehydes with acylsilanes to give 1,3-diol derivs.)

RN 853601-60-2 CAPLUS

CN 1,3-Propanediol, 2,3-diphenyl-1-(trimethylsilyl)-, 1-benzoate, (1S,2S,3R)-rel- (CA INDEX NAME)

Relative stereochemistry.

RN 853601-69-1 CAPLUS

CN 1,3-Propanediol, 1,2-diphenyl-3-(trimethylsilyl)-, (1R,2S,3S)-rel- (CA INDEX NAME)

Relative stereochemistry.

IT 853601-61-3P 853601-62-4P 853601-63-5P

RL: SPN (Synthetic preparation); PREP (Preparation)

(stereoselective tandem aldol-tishchenko reaction of aldehydes with acylsilanes to give 1,3-diol derivs.)

RN 853601-61-3 CAPLUS

CN 1-Naphthalenecarboxylic acid, (1R,2R,3S)-3-hydroxy-3-(1-naphthalenyl)-2-phenyl-1-(trimethylsilyl)propyl ester, rel- (CA INDEX NAME)

Relative stereochemistry.

RN 853601-62-4 CAPLUS

Benzoic acid, 4-cyano-, (1R,2R,3S)-3-(4-cyanophenyl)-3-hydroxy-2-phenyl-1-CN (trimethylsilyl)propyl ester, rel- (CA INDEX NAME)

Relative stereochemistry.

RN 853601-63-5 CAPLUS

Benzoic acid, 4-methoxy-, (1R, 2R, 3S)-3-hydroxy-3-(4-methoxyphenyl)-2-CN phenyl-1-(trimethylsilyl)propyl ester, rel- (CA INDEX NAME)

Relative stereochemistry.

REFERENCE COUNT: THERE ARE 20 CITED REFERENCES AVAILABLE FOR THIS 20 RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L3 ANSWER 10 OF 41 CAPLUS COPYRIGHT 2008 ACS on STN

Immobilization of a platinum catalyst was carried out on the basis of the AB polymer incarcerated (PI) method. The PI platinum catalyst thus prepared showed high activity in hydrosilylation, and recovery and reuse of the catalyst were attained without loss of activity. Application of this catalyst to hydrogenation is also reported.

ACCESSION NUMBER: 2005:308285 CAPLUS

DOCUMENT NUMBER: 143:27005

TITLE: Immobilization of a platinum catalyst using the

polymer incarcerated (PI) method and application to

catalytic reactions

Hagio, Hiroyuki; Sugiura, Masaharu; Kobayashi, Shu AUTHOR(S): CORPORATE SOURCE:

Graduate School of Pharmaceutical Sciences, The

University of Tokyo, Tokyo, 113-0033, Japan

SOURCE: Synlett (2005), (5), 813-816

CODEN: SYNLES; ISSN: 0936-5214

PUBLISHER: Georg Thieme Verlag

DOCUMENT TYPE: Journal LANGUAGE: English

OTHER SOURCE(S): CASREACT 143:27005

IT 852814-20-1P

RL: SPN (Synthetic preparation); PREP (Preparation)

(hydrosilylation and hydrogenation with polymer incarcerated platinum  $\ensuremath{\mathsf{S}}$ 

catalyst)

RN 852814-20-1 CAPLUS

CN Disiloxane, pentamethyl(4-methyl-2,4-diphenylpentyl)- (9CI) (CA INDEX

NAME)

REFERENCE COUNT: 48 THERE ARE 48 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L3 ANSWER 11 OF 41 CAPLUS COPYRIGHT 2008 ACS on STN

A highly regio- and stereoselective method for the synthesis of various AB 2-silylallylboronates (7) from allenes 1 and 2-(dimethylphenylsilyl)-4,4,5,5-tetramethyl[1,3,2]dioxaborolane (5) catalyzed by Pd complexes and initiated by organic iodides is described. Treatment of monosubstituted aryl and alkylallenes RCH:C:CH2 (1a-m) and 1,1-dimethylallene (1n) with borylsilane 5 in the presence of Pd(dba)2 (5 mol %) and 3-iodo-2-methylcyclohex-2-enone (3a) (10 mol %) afforded the corresponding silaboration products 7a-n in moderate to excellent yields. This catalytic silaboration is totally regioselective with the silyl group of 5 adding to the central C and the boryl group to the unsubstituted terminal C of allene. Furthermore, the reactions show very high E stereoselectivity with the Z/E ratios lying in the range from 1/99 to 7/93. In the absence of an organic iodide, silaboration of 1 with 5 still proceeds, but gives products having completely different regiochem. as that of 7. The silaboration chemical can be applied to the synthesis of homoallylic alcs. Treatment of allenes (e.g. PhCH:C:CH2) with borylsilane 5 and aldehydes (e.g. PhCHO) in the presence of Pd(dba)2 (5 mol %) and 3a (10 mol %) at  $80^{\circ}$  in EtOAc for 5 h afforded homoallylic alcs. (e.g. PhCH(OH)CHPhC(SiMe2Ph):CH2) in one pot in good to excellent yields, with exceedingly high syn selectivity (>93%). Mechanistic pathways involving an unusual Pd-catalyzed three-component assembling reaction of dimethylphenylsilyl iodide, allene 1, and borylsilane 5 are proposed to account for these catalytic reactions.

ACCESSION NUMBER: 2004:1048888 CAPLUS

DOCUMENT NUMBER: 142:156052

TITLE: Unusual Palladium-Catalyzed Silaboration of Allenes

Using Organic Iodides as Initiators: Mechanism and

Application

AUTHOR(S): Chang, Kuo-Jui; Rayabarapu, Dinesh Kumar; Yang,

Feng-Yu; Cheng, Chien-Hong

CORPORATE SOURCE: Department of Chemistry, Tsing Hua University,

Hsinchu, 30013, Taiwan

SOURCE: Journal of the American Chemical Society (2005),

127(1), 126-131

CODEN: JACSAT; ISSN: 0002-7863

PUBLISHER: American Chemical Society

DOCUMENT TYPE: Journal English LANGUAGE: OTHER SOURCE(S): CASREACT 142:156052 827575-10-0P, (1S\*,2S\*)-3-[Di(methyl)(phenyl)silyl]-1,2-diphenyl-3buten-1-ol 827575-11-1P, (1S\*,2S\*)-3-[Di(methyl)(phenyl)silyl]-1-(4-methoxyphenyl)-2-phenyl-3-buten-1-ol 827575-12-2P,  $(1S^*, 2S^*) - 1 - (4 - Acetoxyphenyl) - 3 - [di(methyl)(phenyl)silyl] - 2 - phenyl - 3 - buten - 2 - phenyl - 3 - buten - 3$ 1-ol 827575-13-3P,  $(1S^*, 2S^*)-1-(4-Chlorophenyl)-3-$ [di(methyl)(phenyl)silyl]-2-phenyl-3-buten-1-ol 827575-14-4P,  $(1S^*, 2S^*)$  -3-[Di(methyl)(phenyl)silyl]-2-phenyl-1-(4-tolyl)-3-buten-1-ol 827575-15-5P, (1S\*, 2S\*)-1-(4-Acetylphenyl)-3-[di(methyl)(phenyl)silyl]-2-phenyl-3-buten-1-ol 827575-16-6P, (1S\*, 2S\*)-1-(4-Cyanophenyl)-3-[di(methyl)(phenyl)silyl]-2-phenyl-3-buten-1ol 827575-20-2P, (1S\*, 2S\*)-2-(4-Acetylphenyl)-3-[di(methyl)(phenyl)silyl]-1-phenyl-3-buten-1-ol 827575-21-3P, (1S\*, 2S\*)-3-[Di(methyl)(phenyl)silyl]-2-[4-(ethoxycarbonyl)phenyl]-1phenyl-3-buten-1-ol 827575-22-4P, (1S\*,2S\*)-3-[Di(methyl)(phenyl)silyl]-2-(4-methoxyphenyl)-1-phenyl-3-buten-1-ol RL: SPN (Synthetic preparation); PREP (Preparation) (mechanism and application of unusual regioselective/stereoselective palladium-catalyzed silaboration of allenes using organic iodides as initiators) RN 827575-10-0 CAPLUS CN Benzeneethanol,  $\beta$ -[1-(dimethylphenylsilyl)ethenyl]- $\alpha$ -phenyl-,  $(\alpha R, \beta R)$ -rel- (CA INDEX NAME)

Relative stereochemistry.

RN 827575-11-1 CAPLUS CN Benzeneethanol,  $\beta$ -[1-(dimethylphenylsilyl)ethenyl]- $\alpha$ -(4-methoxyphenyl)-,  $(\alpha R, \beta R)$ -rel- (CA INDEX NAME)

Relative stereochemistry.

RN 827575-12-2 CAPLUS CN Benzeneethanol,  $\alpha$ -[4-(acetyloxy)phenyl]- $\beta$ -[1- (dimethylphenylsilyl)ethenyl]-, ( $\alpha$ R, $\beta$ R)-rel- (CA INDEX NAME)

Relative stereochemistry.

RN 827575-13-3 CAPLUS

CN Benzeneethanol,  $\alpha$ -(4-chlorophenyl)- $\beta$ -[1- (dimethylphenylsilyl)ethenyl]-, ( $\alpha$ R,  $\beta$ R)-rel- (CA INDEX NAME)

Relative stereochemistry.

RN 827575-14-4 CAPLUS

CN Benzeneethanol,  $\beta$ -[1-(dimethylphenylsilyl)ethenyl]- $\alpha$ -(4-methylphenyl)-, ( $\alpha$ R, $\beta$ R)-rel- (CA INDEX NAME)

Relative stereochemistry.

RN 827575-15-5 CAPLUS

CN Ethanone, 1-[4-[(1R,2R)-3-(dimethylphenylsilyl)-1-hydroxy-2-phenyl-3-buten-1-yl]phenyl]-, rel- (CA INDEX NAME)

Relative stereochemistry.

RN 827575-16-6 CAPLUS

CN Benzonitrile, 4-[(1R,2R)-3-(dimethylphenylsilyl)-1-hydroxy-2-phenyl-3-buten-1-yl]-, rel- (CA INDEX NAME)

Relative stereochemistry.

RN 827575-20-2 CAPLUS

CN Ethanone, 1-[4-[(1S)-2-(dimethylphenylsilyl)-1-[(S)-hydroxyphenylmethyl]-2-propen-1-yl]phenyl]-, rel- (CA INDEX NAME)

Relative stereochemistry.

RN 827575-21-3 CAPLUS

CN Benzoic acid, 4-[(1R)-2-(dimethylphenylsilyl)-1-[(R)-hydroxyphenylmethyl]-2-propen-1-yl]-, ethyl ester, rel- (CA INDEX NAME)

Relative stereochemistry.

RN 827575-22-4 CAPLUS

CN Benzeneethanol,  $\beta$ -[1-(dimethylphenylsilyl)ethenyl]-4-methoxy- $\alpha$ -phenyl-, ( $\alpha$ R, $\beta$ R)-rel- (CA INDEX NAME)

Relative stereochemistry.

REFERENCE COUNT:

95 THERE ARE 95 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L3 ANSWER 12 OF 41 CAPLUS COPYRIGHT 2008 ACS on STN

AB The cosmetics contain MDxD'y(Dq)zM [I; M = R3Si00.5; D = R2Si0; D' = RR'Si0; Dq = RQSi0; R = (un)substituted hydrocarbyl; R' = 2,4-diphenyl-4-methylpentyl; Q = RaO(C2H4O)p(C3H6O)sRb; Ra = CmH2m; Rb = H, C1-6 alkyl; m = 2-8; p, s = 0-50; p + s ≥1; x = 0-1000; y = 1-100; z = 1-50] manufactured by hydrolysis of silanes containing Me2CPhCH2CHPhCH2SiX2R [X = hydrolyzable group; R = (un)substituted hydrocarbyl], equilibration of the hydrolyzates, reaction with polyorganohydrogensiloxanes, and addition reaction with alkenyl-containing polyethers. The polymers show good compatibility with oils and high water-holding capacity and provide cosmetics with good moisturizing effect, spreadability, luster, and no stickiness. A foundation containing I

[R = Me, Q = (CH2)30(C2H40)6Me, x = 19, y = 12, z = 4] was formulated.

ACCESSION NUMBER: 2004:756362 CAPLUS

DOCUMENT NUMBER: 141:265590

TITLE: Polyether-modified polyorganosiloxanes, their manufacture, and skin cosmetics containing them

INVENTOR(S): Suenaga, Hiroshi; Chen, Hsiang; Kida, Shinji

PATENT ASSIGNEE(S): GE Toshiba Silicone Co., Ltd., Japan

SOURCE: Jpn. Kokai Tokkyo Koho, 20 pp.

CODEN: JKXXAF

DOCUMENT TYPE: Patent LANGUAGE: Japanese

FAMILY ACC. NUM. COUNT: 1

PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 2004256661	A	20040916	JP 2003-48683	20030226
PRIORITY APPLN. INFO.:			JP 2003-48683	20030226

IT 756511-36-1DP, trimethylsilyl-terminated 756819-55-3DP,

trimethylsilyl-terminated

RL: COS (Cosmetic use); PRP (Properties); SPN (Synthetic preparation);

BIOL (Biological study); PREP (Preparation); USES (Uses)

(comprised of actual and assumed monomers; manufacture of polyether-modified polyorganosiloxanes for skin cosmetics)

RN 756511-36-1 CAPLUS

CN Silanediol, methyl-, polymer with dichlorodimethylsilane, dichloromethyl(4-methyl-2,4-diphenylpentyl)silane and  $\alpha$ -methyl-  $\omega$ -(2-propenyloxy)poly(oxy-1,2-ethanediyl), graft (9CI) (CA INDEX NAME)

CM 1

CRN 753002-84-5 CMF C19 H24 C12 Si

CM 2

CRN 43641-90-3 CMF C H6 O2 Si

CM 4

CRN 43641-90-3 CMF C H6 O2 Si

$$\begin{array}{c} \text{OH} \\ | \\ \text{HO-SiH-CH}_3 \end{array}$$

CM 5

CRN 75-78-5 CMF C2 H6 C12 Si

CM 6

CRN 75-21-8 CMF C2 H4 O



L3 ANSWER 13 OF 41 CAPLUS COPYRIGHT 2008 ACS on STN

Title polymers containing siloxane units containing 2,4-diphenyl-4-methylpentyl group on Si are manufactured by hydrolysis of Me2CPhCH2CHPhCH2SiXnR3-n [X = hydrolyzable group; R = (un)substituted hydrocarbyl; n = 1-3] and equilibration of the hydrolyzates. Alternatively, the polymers are manufactured by addition reaction of polyorganohydrogensiloxanes with Me2CPhCH2CHPh:CH2 in the presence of Pt catalysts. Thus, 2,4-diphenyl-4-methylpentyldichlorosilane (sic), Me2SiCl2, and Me3SiCl were hydrolyzed, neutralized, and equilibrated using KOH to give MD25D'25M (M = Me3SiOO.5, D = Me2SiO, D' = MeR'SiO, R' = 2,4-diphenyl-4-methylpentyl) showing refractive index 1.535.

ACCESSION NUMBER: 2004:753450 CAPLUS

DOCUMENT NUMBER: 141:244368

TITLE: Novel polyorganosiloxanes with high refractive index

and their manufacture

INVENTOR(S): Suenaga, Hiroshi; Chen, Qian; Kida, Shinji

PATENT ASSIGNEE(S): GE Toshiba Silicone Co., Ltd., Japan

SOURCE: Jpn. Kokai Tokkyo Koho, 11 pp.

CODEN: JKXXAF

DOCUMENT TYPE: Patent LANGUAGE: Japanese

FAMILY ACC. NUM. COUNT: 1

PATENT INFORMATION:

	 _
JP 2004256660 A 20040916 JP 2003-4868 PRIORITY APPLN. INFO.: JP 2003-4868	 •

IT 753002-86-7DP, trimethylsilyl-terminated

RL: IMF (Industrial manufacture); PRP (Properties); PREP (Preparation) (comprised of actual and assumed monomers; manufacture of polyorganosiloxanes with high refractive index)

RN 753002-86-7 CAPLUS

CN Silanediol, methyl-, polymer with dichlorodimethylsilane and dichloromethyl(4-methyl-2,4-diphenylpentyl)silane (9CI) (CA INDEX NAME)

CM 1

CRN 753002-84-5 CMF C19 H24 C12 Si

CM 2

CRN 43641-90-3 CMF C H6 O2 Si

$$^{\rm OH}_{\rm HO-SiH-CH_3}$$

CM 3

CRN 75-78-5 CMF C2 H6 C12 Si

IT 753002-85-6DP, trimethylsilyl-terminated

RL: IMF (Industrial manufacture); PRP (Properties); PREP (Preparation) (manufacture of polyorganosiloxanes with high refractive index)

RN 753002-85-6 CAPLUS

CN Silane, dichlorodimethyl-, polymer with dichloromethyl(4-methyl-2,4-diphenylpentyl)silane, hydrolytic (9CI) (CA INDEX NAME)

CM 1

CRN 753002-84-5 CMF C19 H24 C12 Si

CM 2

CRN 7732-18-5 CMF H2 O

H<sub>2</sub>O

CM 3

CRN 75-78-5 CMF C2 H6 C12 Si

L3 ANSWER 14 OF 41 CAPLUS COPYRIGHT 2008 ACS on STN

AB PhCMe2CH2CHPhCH2SiXnR3-n [I; X = hydrolyzable group; R = (un)substituted hydrocarbyl; n = 0-3] are manufactured by addition reaction of PhCMe2CH2CHPh:CH2

(II) by HSiXnR3-n (X, R, n = same as I) in the presence of Pt catalysts. Thus, II was hydrosilylated by MeSiHCl2 in PhMe in the presence of chloroplatinic acid at  $70-80^{\circ}$  to give 91.3% I (X = Cl, R = Me, n =

2), which showed refractive index (at  $25^{\circ}$ ) 1.5404.

ACCESSION NUMBER: 2004:753393 CAPLUS

DOCUMENT NUMBER: 141:261190

TITLE: (Diphenylpentyl) silanes for manufacture of

polysiloxanes with high refractive index, and their

manufacture

INVENTOR(S): Suenaga, Hiroshi; Chen, Qian

PATENT ASSIGNEE(S): GE Toshiba Silicone Co., Ltd., Japan

SOURCE: Jpn. Kokai Tokkyo Koho, 8 pp.

CODEN: JKXXAF

DOCUMENT TYPE: Patent LANGUAGE: Japanese

FAMILY ACC. NUM. COUNT: 1

## PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 2004256439	A	20040916	JP 2003-48681	20030226
PRIORITY APPLN. INFO.:			JP 2003-48681	20030226
OFFIED COURSE (C)				

OTHER SOURCE(S): MARPAT 141:261190

753002-84-5P

RL: IMF (Industrial manufacture); PRP (Properties); PREP (Preparation) (manufacture of (diphenylmethylpentyl) silanes by hydrosilylation for polysiloxanes with high refractive index)

753002-84-5 CAPLUS

CN Silane, dichloromethyl(4-methyl-2,4-diphenylpentyl)- (9CI) (CA INDEX NAME)

ANSWER 15 OF 41 CAPLUS COPYRIGHT 2008 ACS on STN

The lithium enolate generated from Me3SiCH2CO2CH(CHMe2)2 (I) with LDA in the presence of (R,R)-1,2-dimethoxy-1,2-diphenylethane addsstereoselectively to acyclic and cyclic  $\alpha, \beta$ -unsatd. ketones to give Michael addition products in up to 74% ee. Addition of the lithium enolate

generated from I with LDA in the presence of (R,R)-1,2-dimethoxy-1,2diphenylethane to (E)-PhCH:CHCOCMe3 yields the Michael addition product in 24% yield and 54% ee along with 32% of the alc. (E)-PhCH:CHCH(OH)CMe3. The use of other chiral ligands such as (-)-sparteine, (R,R)-Me2NCHPhCHPhOCH2CH2OMe, and (S)-4-MeOC6H4OCH2CH(CH2Ph)NMe2 gives the desired Michael addition products in high yields and lower enantioselectivities, while the use of other bases in the deprotonation leads to product in slightly increased yields and with lower enantioselectivities. The use of the nonsilylated ester gives only the product of 1,2-addition 2-Cyclopenten-1-one undergoes enantioselective addition

reactions with the lithium enolate generated from I with LDA in the presence of (R,R)-1,2-dimethoxy-1,2-diphenylethane followed byprotodesilylation to give nonracemic diisopropylcarbinol (R)-2-(3-oxo-1-cyclopentyl) acetate in 47% yield and 74% ee. The use of other chiral ligands yields product in significantly reduced enantioselectivity; the use of either 2-cyclohexen-1-one or 2-cyclohepten-1-one gives Michael addition products either in low yield or not at all.

ACCESSION NUMBER: 2004:144195 CAPLUS

DOCUMENT NUMBER: 140:338953

TITLE: Chiral ligand-controlled asymmetric conjugate addition

of  $\alpha$ -trimethylsilanylacetate to acyclic and

cyclic enones

Iguchi, Mayu; Doi, Hirohisa; Hata, Seiji; Tomioka, AUTHOR(S):

Kiyoshi

CORPORATE SOURCE: Graduate School of Pharmaceutical Sciences, Kyoto

University, Kyoto, 606-8501, Japan

SOURCE: Chemical & Pharmaceutical Bulletin (2004), 52(1),

125-129

CODEN: CPBTAL; ISSN: 0009-2363

PUBLISHER: Pharmaceutical Society of Japan

Journal DOCUMENT TYPE: English LANGUAGE:

OTHER SOURCE(S): CASREACT 140:338953

679835-43-9P

RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)

(chemoselective and enantioselective conjugate addition of a lithium  $\alpha$ -trimethylsilanylacetate ester enolate to  $\alpha$ ,  $\beta$ -unsatd.

acyclic enones in the presence of a nonracemic dimethoxydiphenylethane

ligand)

679835-43-9 CAPLUS RN

Benzenepentanoic acid,  $\delta$ -oxo- $\beta$ -phenyl- $\alpha$ -(trimethylsilyl)-CN , 2-methyl-1-(1-methylethyl)propyl ester (9CI) (CA INDEX NAME)

57 THERE ARE 57 CITED REFERENCES AVAILABLE FOR THIS REFERENCE COUNT: RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

ANSWER 16 OF 41 CAPLUS COPYRIGHT 2008 ACS on STN T.3

AB The nucleophilic addition reaction to acylsilanes, having stereogenic centers at the  $\alpha$  and  $\beta$  positions, derived from the aldol reaction of di-Me acetals and acylsilane silyl enol ethers gives the corresponding  $\alpha$ -silylalcs. in high yields with excellent diastereoselectivity. The protiodesilylation of  $\alpha$ -silylalcs. proceeds with complete retention of the configuration. The reduction of acylsilanes having stereogenic centers at the  $\alpha$  and  $\beta$  positions affords the corresponding  $\alpha$ -silylalcs. in good yields with high diastereoselectivity similarly to the nucleophilic addition And the treatment of acylsilanes having a Ph group on Si atom with F- ion gave Ph carbinol derivs. via migration of the Ph group with high diastereoselectivity.

ACCESSION NUMBER: 2003:746770 CAPLUS

DOCUMENT NUMBER: 139:395991

Diastereoselective alkylation and reduction of TITLE:  $\beta$ -alkoxyacylsilanes: stereoselective construction

of three contiguous stereogenic centers

AUTHOR(S): Honda, Mitsunori; Ohkura, Naoto; Saisyo, Shin-ichi;

Segi, Masahito; Nakajima, Tadashi

Faculty of Engineering, Department of Chemistry and CORPORATE SOURCE:

Chemical Engineering, Kanazawa University, Kanazawa,

920-8667, Japan

SOURCE: Tetrahedron (2003), 59(41), 8203-8212

CODEN: TETRAB; ISSN: 0040-4020

PUBLISHER: Elsevier Science B.V.

DOCUMENT TYPE: Journal LANGUAGE: English

OTHER SOURCE(S): CASREACT 139:395991 482662-09-9 482662-30-6 482662-31-7 ΤT

626235-41-4

RL: RCT (Reactant); RACT (Reactant or reagent)

(diastereoselective nucleophilic addition of organometallic reagents to methoxyacylsilanes to give chiral alpha-silylalcs.)

482662-09-9 CAPLUS RN

CN Silane, [(2R,3S)-3-methoxy-1-oxo-2,3-diphenylpropyl]trimethyl-, rel- (9CI) (CA INDEX NAME)

Relative stereochemistry.

RN 482662-30-6 CAPLUS

CN Silane, [(2R,3S,4R)-3-methoxy-1-oxo-2,4-diphenylpentyl]trimethyl-, rel-(9CI) (CA INDEX NAME)

Relative stereochemistry.

RN 482662-31-7 CAPLUS

CN Silane, [(2R,3R,4S)-3-methoxy-1-oxo-2,4-diphenylpentyl]trimethyl-, rel-(9CI) (CA INDEX NAME)

Relative stereochemistry.

RN 626235-41-4 CAPLUS

CN Silane, [(2R,3R)-3-methoxy-1-oxo-2,3-diphenylpropyl]trimethyl-, rel- (9CI) (CA INDEX NAME)

Relative stereochemistry.

IT 626235-47-0P 626235-48-1P 626235-49-2P

626235-50-5P 626235-51-6P 626235-63-0P

RL: SPN (Synthetic preparation); PREP (Preparation)

(diastereoselective nucleophilic addition of organometallic reagents to methoxyacylsilanes to give chiral alpha-silylalcs.)

RN 626235-47-0 CAPLUS

CN Benzenepropanol,  $\gamma$ -methoxy- $\alpha$ -methyl- $\beta$ -phenyl- $\alpha$ - (trimethylsilyl)-, ( $\alpha$ R,  $\beta$ R,  $\gamma$ R)-rel- (CA INDEX NAME)

Relative stereochemistry.

RN 626235-48-1 CAPLUS

CN Benzenepropanol,  $\gamma$ -methoxy- $\alpha$ -methyl- $\beta$ -phenyl- $\alpha$ - (trimethylsilyl)-, ( $\alpha$ R,  $\beta$ R,  $\gamma$ S)-rel- (CA INDEX NAME)

Relative stereochemistry.

RN 626235-49-2 CAPLUS

CN Benzenepropanol,  $\alpha$ -butyl- $\gamma$ -methoxy- $\beta$ -phenyl- $\alpha$ - (trimethylsilyl)-, ( $\alpha$ R, $\beta$ R, $\gamma$ S)-rel- (CA INDEX NAME)

Relative stereochemistry.

RN 626235-50-5 CAPLUS

CN Benzenepropanol,  $\gamma$ -methoxy- $\alpha$ -(1-methylpropyl)- $\beta$ -phenyl- $\alpha$ -(trimethylsilyl)-, ( $\alpha$ R, $\beta$ R, $\gamma$ S)-rel- (CA INDEX NAME)

Relative stereochemistry.

RN 626235-51-6 CAPLUS

CN Benzenepropanol,  $\gamma$ -methoxy- $\alpha$ ,  $\beta$ -diphenyl- $\alpha$ - (trimethylsilyl)-, ( $\alpha$ R,  $\beta$ S,  $\gamma$ R)-rel- (CA INDEX NAME)

Relative stereochemistry.

RN 626235-63-0 CAPLUS

CN Benzenepropanol,  $\gamma$ -methoxy- $\beta$ -phenyl- $\alpha$ -(trimethylsilyl)-,  $(\alpha R, \beta R, \gamma S)$ -rel- (CA INDEX NAME)

Relative stereochemistry.

IT 626235-59-4P 626235-60-7P

RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)

(diastereoselective nucleophilic addition of organometallic reagents to methoxyacylsilanes to give chiral alpha-silylalcs. and their protodesilylation products)

RN 626235-59-4 CAPLUS

CN Benzenebutanol,  $\gamma$ -methoxy- $\alpha$ ,  $\delta$ -dimethyl- $\beta$ -phenyl- $\alpha$ -(trimethylsilyl)-,  $(\alpha R, \beta R, \gamma S, \delta R)$ -rel- (9CI) (CA INDEX NAME)

Relative stereochemistry.

RN 626235-60-7 CAPLUS

CN Benzenebutanol,  $\gamma$ -methoxy- $\alpha$ ,  $\delta$ -dimethyl- $\beta$ -phenyl- $\alpha$ -(trimethylsilyl)-,  $(\alpha R, \beta R, \gamma R, \delta S)$ -rel- (9CI) (CA INDEX NAME)

Relative stereochemistry.

IT 626235-81-2

RL: RCT (Reactant); RACT (Reactant or reagent)
(protodesilylation reaction of chiral alpha-silylalcs.)

RN 626235-81-2 CAPLUS

CN Silane, [(2R,3S)-3-methoxy-1-oxo-2,3-diphenylpropyl]dimethylphenyl-, rel-(9CI) (CA INDEX NAME)

Relative stereochemistry.

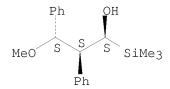
IT 626235-64-1P

RL: SPN (Synthetic preparation); PREP (Preparation) (reduction of acylsilanes having stereogenic centers at the alpha and beta positions affords the corresponding alpha-silylalcs.)

RN 626235-64-1 CAPLUS

CN Benzenepropanol,  $\gamma$ -methoxy- $\beta$ -phenyl- $\alpha$ -(trimethylsilyl)-, ( $\alpha$ R,  $\beta$ R,  $\gamma$ R)-rel- (CA INDEX NAME)

Relative stereochemistry.



REFERENCE COUNT: 38 THERE ARE 38 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L3 ANSWER 17 OF 41 CAPLUS COPYRIGHT 2008 ACS on STN

AB Regioselective hydrozirconation of alkynylsilanes RC.tplbond.CSiMe3 (R = Ph, n-C4H9, n-C5H11) followed by stereoselective Michael addition to  $\alpha$ ,  $\beta$ -unsatd. ketones R1CH:CHC(O)R2 (R1 = Ph, p-NO2C6H4; R2 = Ph, p-CH3OC6H4, m-NO2C6H4, CH3; R1 = R2 = -(CH2)3-) in the presence of CuBr·Me2S produced (Z)- $\gamma$ -silyl- $\gamma$ ,  $\delta$ -unsatd. ketones RCH:C(SiMe3)CH(R1)CH2C(O)R2 (1). The structure of 1 (R = Ph, R1 = p-NO2C6H4, R2 = CH3) was established by X-ray crystallog. Epoxidn. followed by ring-opening hydrolysis of 1 yielded 1,4-diketones RCH2C(O)CH(R1)CH2C(O)R2.

ACCESSION NUMBER: 2002:947459 CAPLUS

DOCUMENT NUMBER: 138:271727

TITLE: Stereoselective preparation of (Z)- $\gamma$ -silyl-

 $\gamma$ ,  $\delta$ -unsaturated ketones and their

application in the synthesis of 1,4-diketones

AUTHOR(S): Zheng, Weixin; Huang, Xian

CORPORATE SOURCE: Department of Chemistry, Zhejiang University,

Hangzhou, 310028, Peop. Rep. China Synthesis (2002), (17), 2497-2502 CODEN: SYNTBF; ISSN: 0039-7881

PUBLISHER: Georg Thieme Verlag

DOCUMENT TYPE: Journal LANGUAGE: English

SOURCE:

OTHER SOURCE(S): CASREACT 138:271727 IT 503299-51-2P 503299-52-3P 503299-56-7P

503299-61-4P 503299-62-5P

RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT

(Reactant or reagent)

(regio- and stereoselective preparation and crystal structure of unsatd. silylketones for diketone synthesis)

RN 503299-51-2 CAPLUS

CN 4-Penten-1-one, 1,3,5-triphenyl-4-(trimethylsilyl)-, (4Z)- (CA INDEX NAME)

Double bond geometry as shown.

RN 503299-52-3 CAPLUS

CN 4-Penten-1-one, 1-(4-methoxyphenyl)-3,5-diphenyl-4-(trimethylsilyl)-, (4Z)- (CA INDEX NAME)

Double bond geometry as shown.

RN 503299-56-7 CAPLUS

CN 4-Nonen-1-one, 1,3-diphenyl-4-(trimethylsilyl)-, (4Z)- (CA INDEX NAME)

Double bond geometry as shown.

RN 503299-61-4 CAPLUS

CN 4-Decen-1-one, 1,3-diphenyl-4-(trimethylsilyl)-, (4Z)- (CA INDEX NAME)

Double bond geometry as shown.

RN 503299-62-5 CAPLUS

CN 4-Decen-1-one, 1-(4-methoxyphenyl)-3-phenyl-4-(trimethylsilyl)-, (4Z)-(CA INDEX NAME)

Double bond geometry as shown.

IT 503299-53-4P 503299-57-8P 503299-58-9P

503299-63-6P

RL: SPN (Synthetic preparation); PREP (Preparation) (regio- and stereoselective preparation and crystal structure of unsatd. silylketones for diketone synthesis)

RN 503299-53-4 CAPLUS

CN 4-Penten-1-one, 1-(3-nitrophenyl)-3,5-diphenyl-4-(trimethylsilyl)-, (4Z)-(CA INDEX NAME)

Double bond geometry as shown.

RN 503299-57-8 CAPLUS

CN 4-Nonen-1-one, 1-(4-methoxyphenyl)-3-phenyl-4-(trimethylsilyl)-, (4Z)- (CA INDEX NAME)

Double bond geometry as shown.

RN 503299-58-9 CAPLUS

CN 4-Nonen-1-one, 1-(3-nitrophenyl)-3-phenyl-4-(trimethylsilyl)-, (4Z)- (CA INDEX NAME)

Double bond geometry as shown.

$$\begin{array}{c|c} \text{O} & \text{Ph} \\ \hline \text{Z} & \text{Bu-n} \\ \\ \text{SiMe3} \end{array}$$

RN 503299-63-6 CAPLUS

CN 4-Decen-1-one, 1-(3-nitrophenyl)-3-phenyl-4-(trimethylsilyl)-, (4Z)- (CA INDEX NAME)

Double bond geometry as shown.

O<sub>2</sub>N 
$$\stackrel{\text{O}}{=}$$
  $\stackrel{\text{Ph}}{=}$   $\stackrel{\text{CH}_2)_4}{=}$  Me  $\stackrel{\text{SiMe}_3}{=}$ 

REFERENCE COUNT: 27 THERE ARE 27 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L3 ANSWER 18 OF 41 CAPLUS COPYRIGHT 2008 ACS on STN

AB The carbocation Et3SiCH2C+Ph(CH:CHPh) is stable at room temperature with tetrakis(pentafluorophenyl)borate as the anion and benzene as the solvent. The cation constitutes the 1st stable  $\beta$ -silyl carbocation in which pos. charge is delocalized both allylically and benzylically.

ACCESSION NUMBER: 2002:678808 CAPLUS

DOCUMENT NUMBER: 138:106758

TITLE: A stable  $\beta$ -silyl carbocation with allyl

conjugation

AUTHOR(S): Lambert, Joseph B.; Liu, Chunqing; Kouliev, Timur CORPORATE SOURCE: Department of Chemistry, Northwestern University,

Evanston, IL, 60208-3113, USA

SOURCE: Journal of Physical Organic Chemistry (2002), 15(9),

667-671

CODEN: JPOCEE; ISSN: 0894-3230

PUBLISHER: John Wiley & Sons Ltd.

DOCUMENT TYPE: Journal LANGUAGE: English

OTHER SOURCE(S): CASREACT 138:106758

IT 485805-21-8P

RL: SPN (Synthetic preparation); PREP (Preparation)

(preparation in the synthesis of the first stable beta-silyl carbocation

with allyl conjugation)

RN 485805-21-8 CAPLUS

CN Silane, (2,4-diphenyl-3-butenyl)triethyl- (9CI) (CA INDEX NAME)

REFERENCE COUNT: 11 THERE ARE 11 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L3 ANSWER 19 OF 41 CAPLUS COPYRIGHT 2008 ACS on STN

AB Treatment of E- or Z-acylsilane silyl enol ethers derived from acylsilanes having an enolizable methylene proton with a mixture of aromatic aldehyde di-Me acetals and TiCl4 in CH2Cl2 gives the corresponding 2,3-anti-3-methoxyacylsilanes in high d.e., independent of the geometry of double bond in acylsilane silyl enol ethers. E.g., aldol reaction of (E)-PhCH:C(OTMS)TMS (E/Z = 96/4) with PhCH(OMe)2 in CH2Cl2 at -78° using TiCl4 as an activating agent afforded the corresponding 2,3-anti-3-methoxyacylsilane PhCH(OMe)CHPhCOTMS (I) (anti/syn = 87/13) in 86% yield with high anti-selectivity after 1 h and likewise

(Z)-PhCH:C(OTMS)TMS (E/Z = 1/99) under the same conditions also gave I (anti/syn = 96/4) in 76% yield. However, E-acylsilane silyl enol ethers react with acetals of aliphatic aldehydes to afford the corresponding aldol adducts with syn-selectivity, while the reaction of Z-isomers provides the products with anti-selectivity. E.g., aldol reaction of PhCH:C(OTMS)TMS (E/Z = 95/5) with H3CCH(OMe)2 under the same conditions as above yielded the corresponding adduct H3CCH(OMe)CH(Ph)COTMS with low syn-selectivity (49/51 = anti/syn) in 52% yield while PhCH:C(OTMS)TMS (E/Z = 15/85) with H3CCH(OMe)2 yielded 64% H3CCH(OMe)CH(Ph)COTMS with high anti-selectivity (anti/syn = 89/11). A mechanism is proposed for the stereoselection observed in these Lewis acid mediated aldol reactions of silyl enol ethers with aldehydes that assumes acyclic extended transition structures.

ACCESSION NUMBER: 2002:641291 CAPLUS

DOCUMENT NUMBER: 138:89850

TITLE: Diastereoselective aldol condensation of acylsilane

silyl enol ethers with acetals

AUTHOR(S): Honda, Mitsunori; Oguchi, Wataru; Segi, Masahito;

Nakajima, Tadashi

CORPORATE SOURCE: Faculty of Engineering, Department of Chemistry and

Chemical Engineering, Kanazawa University, Kanazawa,

920-8667, Japan

SOURCE: Tetrahedron (2002), 58(34), 6815-6823

CODEN: TETRAB; ISSN: 0040-4020

PUBLISHER: Elsevier Science Ltd.

DOCUMENT TYPE: Journal LANGUAGE: English

OTHER SOURCE(S): CASREACT 138:89850 IT 482662-20-4P 482662-24-8P 482662-25-9P 482662-26-0P 482662-30-6P 482662-31-7P

RL: SPN (Synthetic preparation); PREP (Preparation)

(diastereoselective aldol condensation of acylsilane silyl enol ethers

with aromatic and aliphatic acetals)

RN 482662-20-4 CAPLUS

CN Silane, [(2R,3S)-3-methoxy-3-(2-methylphenyl)-1-oxo-2-phenylpropyl]trimethyl-, rel- (9CI) (CA INDEX NAME)

Relative stereochemistry.

RN 482662-24-8 CAPLUS

CN Silane, [(2R,3S)-3-methoxy-1-oxo-2,4-diphenylbutyl]trimethyl-, rel- (9CI) (CA INDEX NAME)

Relative stereochemistry.

RN 482662-25-9 CAPLUS

CN Silane, [(2R,3R)-3-methoxy-1-oxo-2,4-diphenylbutyl]trimethyl-, rel- (9CI) (CA INDEX NAME)

Relative stereochemistry.

RN 482662-26-0 CAPLUS

CN 1-Propanol, 3-[(1R,2S)-3-oxo-1,2-diphenyl-3-(trimethylsilyl)propoxy]-, rel- (CA INDEX NAME)

Relative stereochemistry.

RN 482662-30-6 CAPLUS

CN Silane, [(2R,3S,4R)-3-methoxy-1-oxo-2,4-diphenylpentyl]trimethyl-, rel-(9CI) (CA INDEX NAME)

Relative stereochemistry.

RN 482662-31-7 CAPLUS

CN Silane, [(2R,3R,4S)-3-methoxy-1-oxo-2,4-diphenylpentyl]trimethyl-, rel-(9CI) (CA INDEX NAME)

Relative stereochemistry.

IT 482662-09-9P

RL: SPN (Synthetic preparation); PREP (Preparation) (diastereoselective aldol condensation of acylsilane silyl enol ethers with aromatic and aliphatic acetals and its mechanism)

RN 482662-09-9 CAPLUS

CN Silane, [(2R,3S)-3-methoxy-1-oxo-2,3-diphenylpropyl]trimethyl-, rel- (9CI) (CA INDEX NAME)

Relative stereochemistry.

REFERENCE COUNT: 48 THERE ARE 48 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L3 ANSWER 20 OF 41 CAPLUS COPYRIGHT 2008 ACS on STN

AB 2-Phenylpropene was hydrosilylated using dichloromethylsilane in the presence of H2PtC16 synthesizing dichloromethyl(2-phenylpropyl)silane. The latter reacted with methanol in the presence of carbamide obtaining dimethoxymethyl(2-phenylpropyl)silane, whose reaction with methylmagnesium iodide gave methoxydimethyl(2-phenylpropyl)silane. Treatment of the latter with 40% HF gave fluorodimethyl(2-phenylpropyl)silane which reacted with BrMgC.tplbond.CH yielding dimethylethynyl(2-phenylpropyl)silane.

ACCESSION NUMBER: 2001:317259 CAPLUS

DOCUMENT NUMBER: 135:76929

TITLE: Hydrosilylation of 2-phenylpropene with

dichloromethylsilane and transformations of the

resulting adduct

AUTHOR(S): Yarosh, O. G.; Burnashova, T. D.; Yarosh, N. K.;

Voronkov, M. G.

CORPORATE SOURCE: Irkutsk Institute of Chemistry, Siberian Division,

Russian Academy of Sciences, Irkutsk, Russia

SOURCE: Russian Journal of General Chemistry (Translation of

Zhurnal Obshchei Khimii) (2000), 70(10), 1555-1556

CODEN: RJGCEK; ISSN: 1070-3632

PUBLISHER: MAIK Nauka/Interperiodica Publishing

DOCUMENT TYPE: Journal LANGUAGE: English

OTHER SOURCE(S): CASREACT 135:76929

C1

IT 347194-20-1P

RL: SPN (Synthetic preparation); PREP (Preparation)

(hydrosilylation of 2-phenylpropene with dichloromethylsilane and

transformations of the resulting adduct)

RN 347194-20-1 CAPLUS

CN Silane, dichloromethyl(2-methyl-2,4-diphenylpentyl)- (9CI) (CA INDEX NAME)

Ph

REFERENCE COUNT:

THERE ARE 4 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L3 ANSWER 21 OF 41 CAPLUS COPYRIGHT 2008 ACS on STN

AB Polysiloxanes have units of [-SiMe(OR1)0-]a and/or [-SiMe(CH2)tSi(OR1)3]0-]a in combination with [-SiMe[CH2CHMeCH2(CMe2CH2)rH]0-]b or [-SiMe[(CH2)30(R20)5R3]0-]c, wherein R1 = C1-6 alkyl, C1-21 acyl; R2 = C2-4 alkylene; R3 = hydrocarbyl; a = 1-200; b = 1-200; c = 1-200; t = 2,

3; s = 1-100. Siloxane-based reactive plasticizers have both at least one plasticizing moiety selected from organic groups having an ester linkage and aliphatic and aromatic hydrocarbon groups and at least one reactive group selected from alkoxysilyl groups and acyloxysilyl groups, the plasticizing moiety accounting for at least 50% of the plasticizer. A rubber composition comprised natural rubber 100, carbon black 50, alkenyl-terminated polyisobutylene-modified polysiloxane 20, ZnO 3, stearic acid 1, antioxidant 1, oil-treated S powder 1.7, and accelerator CZ 1.0 part.

ACCESSION NUMBER: 1998:485111 CAPLUS

DOCUMENT NUMBER: 129:123690

TITLE: Modified polysiloxanes, rubber compositions and tire

tread rubber compositions containing the same with good wear and ice and wet skid resistance, and

reactive plasticizers

INVENTOR(S): Ishikawa, Kazunori; Yatsuyanagi, Fumito PATENT ASSIGNEE(S): The Yokohama Rubber Co., Ltd., Japan

SOURCE: PCT Int. Appl., 52 pp.

CODEN: PIXXD2

DOCUMENT TYPE: Patent LANGUAGE: Japanese

FAMILY ACC. NUM. COUNT: 1

PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.		DATE
WO 9829473 W: US	A1	19980709	WO 1997-JP4899		19971226
RW: AT, BE, CH,	DE, DK	, ES, FI,	FR, GB, GR, IE, IT,	LU, MO	C, NL, PT, SE
JP 11080551	A	19990326	JP 1997-272826		19971006
JP 11106512	A	19990420	JP 1997-357767		19971225
EP 890598	A1	19990113	EP 1997-949259		19971226
R: DE, FR, IT					
US 6140450	A	20001031	US 1998-125818		19980826
PRIORITY APPLN. INFO.: JP 1996-349658 A 19961227					
			JP 1997-92316	A	19970410
			JP 1997-194313	A	19970718
			JP 1997-213359	A	19970807
			JP 1997-272826	A	19971006
			WO 1997-JP4899	W	19971226

IT 210175-32-9D, trimethylsilyl-terminated

RL: DEV (Device component use); POF (Polymer in formulation); USES (Uses) (modified polysiloxanes, rubber compns. and tire tread rubber compns. containing the same with good wear and ice and wet skid resistance, and reactive plasticizers)

RN 210175-32-9 CAPLUS

CN Silanediol, methyl(4-methyl-2,4-diphenylpentyl)-, polymer with methyl[2-(trimethoxysilyl)ethyl]silanediol (9CI) (CA INDEX NAME)

CM 1

CRN 210175-31-8 CMF C19 H26 O2 Si

CM 2

CRN 161174-84-1 CMF C6 H18 O5 Si2

REFERENCE COUNT: 2 THERE ARE 2 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L3 ANSWER 22 OF 41 CAPLUS COPYRIGHT 2008 ACS on STN

AΒ The reaction of the substituted vinylsilanes (Me3Si) 2C:CH2, (Z)-Me3SiCH:CHPh, Me3SiPhC:CH2, Me3Si(Me3C)C:CH2, (Me3Si)2C:CHPh, (Me3Si)2C:CHCMe3, (Me3Si)2C:CHCMePh2, and (Me3Si)2C:CHCMe2Ph with Li was studied. Depending on the substituents on the vinylsilane and the solvent employed, several new reaction pathways are observed, which were proved by independent syntheses of the reactive intermediates (E)-Me3SiCLi:CHPh, (Me3Si)2C:CHLi, Me3SiLi2CCHLiPh, 2-LiC6H4CHLiCHLiSiMe3, and (E)-2-LiC6H4CH:CLiSiMe3. Thus, besides the known elimination of LiH, either a 1,4-H shift of Me3SiLi2CCHLiPh to 2-LiC6H4CHLiCHLiSiMe3 or a Grovenstein-Zimmerman rearrangement of (Me3Si)2LiCCHLiCMePh2 to (Me3Si)2LiCCHPhCLiMePh can occur as follow-up reactions. Also, 2 different types of dimerization of the silyl-substituted vinyllithium compds. were identified. Either (Me3Si)2C:CHLi adds to the starting vinylsilane leading to (Me3Si)2C:CHCH2CLi(SiMe3)2, or Li metal-catalyzed dimerization to (Me3Si)2LiCCH:CHCLi(SiMe3)2 takes place, which is without precedence.

ACCESSION NUMBER: 1998:455569 CAPLUS

DOCUMENT NUMBER: 129:202974

TITLE: Polylithiumorganic compounds. Part 24. The reaction of

substituted vinylsilanes with lithium metal

AUTHOR(S): Maercker, Adalbert; Reider, Kerstin; Girreser, Ulrich

CORPORATE SOURCE: Institut Organische Chemie, Universitaet-GH Siegen,

Siegen, D-57068, Germany

SOURCE: European Journal of Organic Chemistry (1998), (7),

1455-1465

CODEN: EJOCFK; ISSN: 1434-193X

PUBLISHER: Wiley-VCH Verlag GmbH

DOCUMENT TYPE: Journal LANGUAGE: English

OTHER SOURCE(S): CASREACT 129:202974 IT 211987-05-2P 211987-15-4P 211987-16-5P

RL: SPN (Synthetic preparation); PREP (Preparation)

(preparation of polylithiumorg. compds. by reaction of vinylsilanes with

lithium metal) N 211987-05-2 CAPLUS

RN 211987-05-2 CAPLUS CN Lithium,  $[\mu-[1-methyl-1,2-diphenyl-3,3-bis(trimethylsilyl)-1,3-propanediyl]]di- (9CI) (CA INDEX NAME)$ 

RN 211987-15-4 CAPLUS
CN Silane, [(2S,3R)-2,3-diphenylbutylidene]bis[trimethyl- (9CI) (CA INDEX NAME)

Relative stereochemistry.

RN 211987-16-5 CAPLUS

CN Silane, [(2R,3R)-2,3-diphenylbutylidene]bis[trimethyl- (9CI) (CA INDEX NAME)

Relative stereochemistry.

L3 ANSWER 23 OF 41 CAPLUS COPYRIGHT 2008 ACS on STN GI

$$\begin{array}{c|c}
R^1 & R^3 \\
\hline
 & X & CO_2 \\
\hline
 & R^4 & CO_2 \\
\hline
 & SiR^5R^6 (OSiR^5R^6)_nR^7
\end{array}$$

AB The photoreceptor has a photosensitive layer whose surface contains a polycarbonate-based polymer having a repeating units I [R1-4 = halo. alkyl, aryl; R5-7 = alkyl, aryl; X = alkylene (ester), alkylenecarbonyl; n = 0-1000] and II (R8-15 = halo, alkoxy, alkyl, alkenyl, aryl; Y = CR16R17, S, S02, (CH2)a, O, (CH2)a(SiR16R17O)bSiR16R17(CH2)a; R16, R17 = H, halo, alkyl, aryl; R16 and R17 may form a heterocyclic or ring) on an elec. conductive support. The cartridge and the apparatus having the photoreceptor

are also claimed. The photoreceptor shows good mech. strength and

improved solvent crack resistance.

ACCESSION NUMBER: 1997:526323 CAPLUS

DOCUMENT NUMBER: 127:240966

TITLE: Electrophotographic photoreceptor, process cartridge

having it, and electrophotographic apparatus

INVENTOR(S): Anayama, Hideki; Hirano, Hidetoshi

PATENT ASSIGNEE(S): Canon K. K., Japan

SOURCE: Jpn. Kokai Tokkyo Koho, 14 pp.

CODEN: JKXXAF

DOCUMENT TYPE: Patent LANGUAGE: Japanese

FAMILY ACC. NUM. COUNT: 1

PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 09204058	A	19970805	JP 1996-11453	19960126
PRIORITY APPLN. INFO.:			JP 1996-11453	19960126

IT 195252-92-7P 195252-96-1P 195252-98-3P

RL: DEV (Device component use); IMF (Industrial manufacture); PREP (Preparation); USES (Uses)

(electrophotog. photoreceptor containing polycarbonate-containing photosensitive layer with solvent crack resistance)

RN 195252-92-7 CAPLUS

CN Carbonic dichloride, polymer with  $\alpha-[[2,4-bis(4-hydroxyphenyl)pentyl]dimethylsilyl]-<math>\omega-[(trimethylsilyl)oxy]poly[oxy(dimethylsilylene)]$  and 4,4'-(1-methylethylidene)bis[phenol] (9CI) (CA INDEX NAME)

CM 1

CRN 170441-84-6

CMF (C2 H6 O Si)n C22 H34 O3 Si2

CCI PMS

CM 2

CRN 80-05-7 CMF C15 H16 O2

CM 3

CRN 75-44-5 CMF C C12 O

RN 195252-96-1 CAPLUS

CN Carbonic dichloride, polymer with  $\alpha-[[2,4-bis(4-hydroxyphenyl)pentyl]dimethylsilyl]-<math>\omega-[(trimethylsilyl)oxy]poly[oxy(dimethylsilylene)]$  and 4,4'-cyclohexylidenebis[phenol] (9CI) (CA INDEX NAME)

CM 1

CRN 170441-84-6

CMF (C2 H6 O Si)n C22 H34 O3 Si2

CCI PMS

CM 2

CRN 843-55-0 CMF C18 H20 O2

CM 3

CRN 75-44-5 CMF C C12 O

RN 195252-98-3 CAPLUS

CN Carbonic dichloride, polymer with  $\alpha-[[2,4-bis(4-hydroxyphenyl)pentyl]dimethylsilyl]-<math>\omega-[(trimethylsilyl)oxy]poly[oxy(dimethylsilylene)]$  and 4,4'-(1-methylethylidene)bis[2-methylphenol] (9CI) (CA INDEX NAME)

CM 1

CRN 170441-84-6

CMF (C2 H6 O Si)n C22 H34 O3 Si2

CCI PMS

CM 2

CRN 79-97-0 CMF C17 H20 O2

CM 3

CRN 75-44-5 CMF C C12 O

IT 170441-84-6P

RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)

(monomer; electrophotog. photoreceptor containing polycarbonate-containing photosensitive layer with solvent crack resistance)

RN 170441-84-6 CAPLUS

CN Poly[oxy(dimethylsilylene)],  $\alpha$ -[[2,4-bis(4-hydroxyphenyl)pentyl]dimethylsilyl]- $\omega$ -[(trimethylsilyl)oxy]- (9CI) (CA INDEX NAME)

L3 ANSWER 24 OF 41 CAPLUS COPYRIGHT 2008 ACS on STN

AΒ The title compns., which are useful for adhesion of acrylic or ABS resins, contain (A) 100 parts siloxanes bearing (R1)aSiO(4-a)/2 [R1 = C1-10 (halo)hydrocarbyl;  $1.8 \le a < 2.3$ ] units and  $\ge 2$  aliphatic unsatd. groups, and having viscosity 10-10,000,000 cP at 25°; (B) 0-30 parts H siloxanes bearing (R2)bHcSiO(4-b-c)/2 [R2 = C1-10 (halo)hydrocarbyl; 1.6 < b < 2.2;  $0.002 \le c \le 1$ ; 1.8 < b + c  $\leq$  3.0] units and  $\geq$ 2 Si-H groups; (C) 0.1-30 parts organosilicons containing  $\geq 2$  olefinic monomer units and  $\geq 1$  Si-H group (total Si-H of B and C is 0.4-10 mol/mol-total aliphatic unsatd. group) and having softening point or m.p.  $\leq 120^{\circ}$ ; and (D) 1-2000 ppm Pt-group metal compds. Thus, 500 mL 0.5 mol/L  $\alpha$ -methylstyrene in THF was reacted with 20 g allyl chloride in the presence of a Na mirror at room temperature to  $40^{\circ}$  for 6 h and treated with 250 g 1,3,5,7-tetramethylcyclotetrasiloxane at 100° for 2 h to prepare an organosilicon compound A composition containing dimethylvinylsilyl-terminated di-Me

siloxane 120, aerosol SiO2 40, hexamethyldisilazane 8, H2O 1, Me3Si-terminated Me H siloxane 3, vinyl Me polysiloxane 4, and 3-methyl-3-hydroxy-1-butyne 0.1 part was mixed with 50 ppm Pt-vinyl siloxane complex and 0.5% of the above organosilicon compound and cured to prepare a test piece showing good adhesion with polycarbonates, ABS resin, acrylic resins, and polystyrene.

ACCESSION NUMBER: 1997:69666 CAPLUS

DOCUMENT NUMBER: 126:90426

TITLE: Addition-curable silicone rubber adhesive compositions

INVENTOR(S):
Fujiki, Hironao

PATENT ASSIGNEE(S): Shinetsu Chemical Industry Co., Ltd., Japan

SOURCE: Jpn. Kokai Tokkyo Koho, 10 pp.

CODEN: JKXXAF

DOCUMENT TYPE: Patent LANGUAGE: Japanese

FAMILY ACC. NUM. COUNT: 1

PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
 JР 08291254	 A	19961105	JP 1995-96593	19950421
JP 3174713	В2	20010611		
PRIORITY APPLN. INFO.: 185517-16-2P			JP 1995-96593	19950421

RL: IMF (Industrial manufacture); MOA (Modifier or additive use); PREP (Preparation); USES (Uses)

(adhesion promoters; addition-curable silicone rubber adhesive compns.)

RN 185517-16-2 CAPLUS

CN Trisiloxane, 3-[(dimethylsilyl)oxy]-1,1,5,5-tetramethyl-3-(4-methyl-2,4-diphenylpentyl)- (CA INDEX NAME)

L3 ANSWER 25 OF 41 CAPLUS COPYRIGHT 2008 ACS on STN

AΒ Treatment of N-(toluene-p-sulfonyl)vinylsulfoximines TolSO2N:S(O)PhCH:CHR [R = Ph, Me, CHMe2, cyclohexyl, Ph(CH2)2, Bu, Tol = 4-MeC6H4] with methyllithium at  $-78^{\circ}$ , followed by addition of chlorotrimethylsilane, results in the efficient formation of  $\alpha$ -silyl vinylsulfoximines TolSO2N:S(O)PhC(SiMe3):CHR (I) in good to excellent yield. Nucleophilic addition of a range of simple alkyl and aryl organometallics (lithium, copper-lithium and Grignard reagents) occurs in variable yield to give the Michael adducts TolSO2N:S(O)PhCH(SiMe3)CHRR1 (R1 = Bu, Me, Ph), with organolithium reagents being most effective. The degree of stereoselectivity of each of the addition reactions was determined by 1H NMR of the desilylated products TolSO2N:S(O)PhCH2CHRR1 (II), and proved to be synthetically useful for compds. in which the starting lpha-silylvinylsulfoximines were branched at the  $\gamma$ -position, and also when phenyllithium was used as the nucleophile. The sense of stereoselectivity was determined in two cases by X-ray crystal structure anal. of II (R = CHMe2, R1 = Me; R = cyclohexyl, R1 = Ph). A one-pot process for the conversion of  $\alpha$ -silylvinylsulfoximines I (R = CHMe2, cyclohexyl) to  $\alpha$ -substituted carboxylic acids (2R)-HO2CCHRR' (R' = Me, Bu) was developed, using an in situ phenylselenation-oxidation process following the initial conjugate addition Use of enantiomerically pure starting materials allowed the assignment configuration of two carboxylic acids by comparison with literature data, and hence indirectly of the relative stereochem. of the initial Michael adducts II (R = CHMe2, R1 = Me; R = cyclohexyl, R1 = Me).

ACCESSION NUMBER: 1996:454512 CAPLUS

DOCUMENT NUMBER: 125:221280

TITLE: Stereoselective addition of organometallic reagents of

N-(tosyl)vinylsulfoximines

AUTHOR(S): Jackson, Richard F. W.; Briggs, Andrew D.; Brown, Paul

A.; Clegg, William; Elsegood, Mark R. J.; Frampton,

Christopher

CORPORATE SOURCE: Dep. Chem., Univ. Newcastle, Newcastle upon Tyne, NE1

7RU, UK

SOURCE: Journal of the Chemical Society, Perkin Transactions

1: Organic and Bio-Organic Chemistry (1996), (14),

1673-1682

CODEN: JCPRB4; ISSN: 0300-922X

PUBLISHER: Royal Society of Chemistry

DOCUMENT TYPE: Journal LANGUAGE: English

IT 181268-71-3P

RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)

(stereoselective addition of organometallic compds. to N-(tosyl)vinylsulfoximines)

RN 181268-71-3 CAPLUS

CN Sulfoximine, S-[2,4-diphenyl-1-(trimethylsilyl)butyl]-N-[(4-methylphenyl)sulfonyl]-S-phenyl- (9CI) (CA INDEX NAME)

L3 ANSWER 26 OF 41 CAPLUS COPYRIGHT 2008 ACS on STN GI

AΒ The polycarbonates with intrinsic viscosity  $(\eta) \le 2.0 \text{ dL/g}$ comprise (A) 0.01-50% siloxane group-containing bisphenyl repeating units I and (B) bisphenyl repeating units II [R1-4 = H, halo, (substituted)] alkyl, aryl; R5-9 = alkyl, aryl; X = alkylene, alkylene ester, alkylenecarbonyl; n = 0-1000; R10-17 = H, halo, alkoxy, (substituted) alkyl, alkenyl, (substituted) aryl; Y = CR18CR19, S, SO2, (CH2)a, O, (CH2)a(SiR18R190)bSiR18R19(CH2)a; R18, R19 = H, halo, (substituted) alkyl, aryl; R18 and R19 may form a carbocycle or heterocycle; a, b  $\geq 0$ ]. Thus, 26.8 g 4-methyl-2,4-bis(hydroxyphenyl)-1-pentene and 274 g MeSiH(OSiMe2)36Me were heated at 110° for 3 h in the presence of chloroplatinic acid to give a siloxane-containing bisphenol, 10.2 g of which was treated with 2,2-bis(4-hydroxyphenyl)propane 91.2, p-tert-butylphenol 1.44, and COCl2 51 g at  $15^{\circ}$  for 2 h with emulsification to give a polymer with  $\eta$  0.65 dL/g (0.5 g/dL in CH2Cl2 at 20°). The polymer was press-molded to obtain a test piece showing total light transmittance 90.3% and good abrasion resistance.

Ι

ACCESSION NUMBER: 1995:795576 CAPLUS

DOCUMENT NUMBER: 123:314941

TITLE: Polycarbonates containing polysiloxane structures and

their manufacture

INVENTOR(S): Ogawa, Noryoshi; Tajima, Jun

PATENT ASSIGNEE(S): Mitsubishi Gas Chemical Co., Japan

SOURCE: Jpn. Kokai Tokkyo Koho, 9 pp.

CODEN: JKXXAF

DOCUMENT TYPE: Patent LANGUAGE: Japanese

FAMILY ACC. NUM. COUNT: 1

PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 07165897	A B2	19950627	JP 1993-311833	19931213
JP 3371922	BZ	20030127		
PRIORITY APPLN. INFO.:			JP 1993-311833	19931213

IT 170441-85-7P 170441-88-0P 170441-89-1P

RL: IMF (Industrial manufacture); PRP (Properties); TEM (Technical or engineered material use); PREP (Preparation); USES (Uses)

RN 170441-85-7 CAPLUS

CN Carbonic dichloride, polymer with  $\alpha-[[2,4-bis(4-hydroxyphenyl)pentyl]dimethylsilyl]-<math>\omega-[(trimethylsilyl)oxy]poly[oxy(dimethylsilylene)]$  and 4,4'-(1-methylethylidene)bis[phenol], graft (9CI) (CA INDEX NAME)

CM 1

CRN 170441-84-6

CMF (C2 H6 O Si)n C22 H34 O3 Si2

CCI PMS

CM 2

CRN 80-05-7 CMF C15 H16 O2

CM 3

CRN 75-44-5 CMF C C12 O

RN 170441-88-0 CAPLUS

CN Carbonic dichloride, polymer with  $\alpha-[[2,4-bis(4-hydroxyphenyl)pentyl]dimethylsilyl]-<math>\omega-[(trimethylsilyl)oxy]poly[oxy(dimethylsilylene)]$  and 4,4'-cyclohexylidenebis[phenol], graft (9CI) (CA INDEX NAME)

CM 1

CRN 170441-84-6

CMF (C2 H6 O Si)n C22 H34 O3 Si2

CCI PMS

CM 2

CRN 843-55-0 CMF C18 H20 O2

CM 3

CRN 75-44-5 CMF C C12 O

RN 170441-89-1 CAPLUS

CN Carbonic dichloride, polymer with  $\alpha\text{-[[2,4-bis(4-$ 

hydroxyphenyl)pentyl]dimethylsilyl]- $\omega$ -[(trimethylsilyl)oxy]poly[oxy(dimethylsilylene)] and 4,4'-(1-methylethylidene)bis[2-methylphenol], graft (9CI) (CA INDEX NAME)

CM 1

CRN 170441-84-6

CMF (C2 H6 O Si)n C22 H34 O3 Si2

CCI PMS

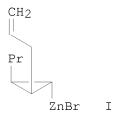
CM 2

CRN 79-97-0 CMF C17 H20 O2

CM 3

CRN 75-44-5 CMF C C12 O

L3 ANSWER 27 OF 41 CAPLUS COPYRIGHT 2008 ACS on STN GI



AB 1,1- Or n,n-bismetallic reagents bearing a methoxymethyl ether in the  $\gamma$  position undergo cyclization at room temperature to give monometalated, diastereoselectively substituted cyclopropanes, e.g., I. The nature of the substituents is crucial for this diastereoselection, a  $\pi$ -chelation between one metal and a properly located unsatn., as well as 1,2-strain, probably explain the steric outcome of these reactions.

ACCESSION NUMBER: 1995:495382 CAPLUS

DOCUMENT NUMBER: 123:82859

TITLE: Stereodefined Substituted Cyclopropyl Zinc Reagents

from Gem-Bismetallics

AUTHOR(S): Beruben, Dov; Marek, Ilane; Normant, Jean F.; Platzer,

Nicole

CORPORATE SOURCE: Laboratoire de Chimie des Organoelements, Universite

P. et M. Curie, Paris, 75252, Fr.

SOURCE: Journal of Organic Chemistry (1995), 60(8), 2488-501

CODEN: JOCEAH; ISSN: 0022-3263

PUBLISHER: American Chemical Society

DOCUMENT TYPE: Journal LANGUAGE: English

OTHER SOURCE(S): CASREACT 123:82859

IT 165268-84-8P 165268-85-9P

RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)

(preparation of chiral cyclopropanes via cyclization of bismetallic reagents

bearing a methoxymethyl ether in the  $\gamma$  position)

RN 165268-84-8 CAPLUS

CN Benzeneethanol,  $\alpha$ -phenyl- $\beta$ -[1-(trimethylsilyl)ethenyl]-, (R\*,R\*)- (9CI) (CA INDEX NAME)

Relative stereochemistry.

RN 165268-85-9 CAPLUS

CN Silane, [3-(methoxymethoxy)-1-methylene-2,3-diphenylpropyl]trimethyl-, (R\*,R\*)- (9CI) (CA INDEX NAME)

Relative stereochemistry.

L3 ANSWER 28 OF 41 CAPLUS COPYRIGHT 2008 ACS on STN

AB The replacement of the usual electron donating alkyl groups on silicon, with electroneg. chloride ligands, changes the mechanism and outcome of the reaction of  $(E)-\beta-(\text{dichlorobenzylsilyl})$  styrene with proton and carbon electrophiles. Electrophilic addition rather than the usual substitution occurs, so that the silicon remains intact to mediate further chemical reactions. The exptl. results show that Friedel-Crafts reactions of the silylated alkene are subject to the same limitations observed for non-silylated alkenes; the extent of polymerization increases as the stability

of the carbenium ion decreases.

ACCESSION NUMBER: 1994:509734 CAPLUS

DOCUMENT NUMBER: 121:109734

ORIGINAL REFERENCE NO.: 121:19853a, 19856a

TITLE: Electrophilic addition to styrylsilanes: sequential

carbon-carbon bond forming reactions

AUTHOR(S): Henry, Courtney; Jueschke, Ralf; Brook, Michael A.

CORPORATE SOURCE: Department of Chemistry, McMaster University,

Hamilton, ON, L8S 4M1, Can.

SOURCE: Inorganica Chimica Acta (1994), 220(1-2), 145-54

CODEN: ICHAA3; ISSN: 0020-1693

DOCUMENT TYPE: Journal LANGUAGE: English IT 156970-68-2P 156970-69-3P

RL: PRP (Properties); SPN (Synthetic preparation); PREP (Preparation)

(preparation and NMR spectra of)

RN 156970-68-2 CAPLUS

CN Silane, [1-[(2-methylphenyl)phenylmethyl]-2-phenyl-1,3-propanediyl]bis[trichloro- (9CI) (CA INDEX NAME)

RN 156970-69-3 CAPLUS

CN Silane, [1-[(4-methylphenyl)phenylmethyl]-2-phenyl-1,3-propanediyl]bis[trichloro- (9CI) (CA INDEX NAME)

L3 ANSWER 29 OF 41 CAPLUS COPYRIGHT 2008 ACS on STN

 $R4(PrO)4(\mu-PrO)2W2$  (3; R = Me, Et, Pr, Bu, sec-Bu, iso-Bu, hexyl, AB Me3SiCH2, Ph) prepared in situ by reaction of organolithium or Grignard compds. with (PrO)4( $\mu$ -PrO)2W2Cl4 (2), react with aromatic aldehydes or ketones and with the  $\alpha$ ,  $\beta$ -unsatd. ketone benzylideneacetone in a novel reaction, called the ARCD (additive, reductive carbonyl dimerization) reaction, to give RR'R"CCR'R" (4; same R; R' = e.g., H, Me, Ph; R" = e.g., Ph) in mostly good yields. In the case of benzylideneacetone and furfural, rearranged products are formed in addition to the ARCD products. With Ph4(PrO)4( $\mu$ -PrO)2W2 (3b), ARCD reactions are also possible in moderate yields with aliphatic aldehydes and ketones. The more closely investigated reagent  $Me4(PrO)4(\mu-PrO)2W2$  (3a; decomposition at about  $-45^{\circ}$ ) tolerates the aromatic bound functional groups Cl, F, OH, OMe, and NMe2 in the substrates, but not NO2 and CO2Et substituents. It reacts with PhCOX (X = OEt, Cl, OCOPh) via acetophenone to give PhCMe2CMe2Ph. A radical mechanism is postulated for the ARCD reactions.

ACCESSION NUMBER: 1994:322299 CAPLUS

DOCUMENT NUMBER: 120:322299

ORIGINAL REFERENCE NO.: 120:56689a,56692a

TITLE: Organomolybdenum and organotungsten reagents. V. On

the additive, reductive carbonyl dimerization (ARCD

reaction)

AUTHOR(S): Kauffmann, Thomas; Jordan, Jan; Voss, Karl Uwe; Wilde,

Heinz Wilhelm

CORPORATE SOURCE: Org. Chem. Inst., Univ. Muenster, Muenster, D-48149,

Germany

SOURCE: Chemische Berichte (1993), 126(9), 2083-91

CODEN: CHBEAM; ISSN: 0009-2940

DOCUMENT TYPE: Journal LANGUAGE: German

OTHER SOURCE(S): CASREACT 120:322299

IT 41115-16-6P

RN

RL: SPN (Synthetic preparation); PREP (Preparation)

(preparation of)

CN Silane, (2,3-diphenyl-1,4-butanediyl)bis[trimethyl- (9CI) (CA INDEX NAME)

L3 ANSWER 30 OF 41 CAPLUS COPYRIGHT 2008 ACS on STN

AB A wide range of unsatd. aryl-, alkenyl-, and alkynylcopper compds. can be selectively homologated by a methylene unit using (iodomethyl)zinc iodide or bis(iodomethyl)zinc. These reactions allow the generation of mixed allylic zinc-copper compds. which can be efficiently trapped with carbonyl compds. An application to a general preparation of functionalized  $\alpha$ -methylene- $\gamma$ -butyrolactones is described. The homologation of alkynylcoppers with (iodomethyl)zinc iodide allows a one-pot preparation of propargylic copper reagents which in the presence of a carbonyl compound provide various homopropargylic alcs. in excellent yields. In the absence of an electrophile, a clean quadruple methylene homologation of alkynylcopper occurs to furnish dienic copper reagents. The homologation of other types of copper reagents is also possible, and carbanions at the  $\alpha$ -position to amines as well as homoenolates of aldehydes or ketones can also be prepared by this method.

ACCESSION NUMBER: 1993:448724 CAPLUS

DOCUMENT NUMBER: 119:48724

ORIGINAL REFERENCE NO.: 119:8819a,8820a

TITLE: Selective mono- and polymethylene homologations of

copper reagents using (iodomethyl)zinc iodide

AUTHOR(S): Sidduri, AchyuthaRao; Rozema, Michael J.; Knochel,

Paul

Dep. Chem., Univ. Michigan, Ann Arbor, MI, 48109-1055, CORPORATE SOURCE:

USA

Journal of Organic Chemistry (1993), 58(10), 2694-713 SOURCE:

CODEN: JOCEAH; ISSN: 0022-3263

DOCUMENT TYPE: Journal English LANGUAGE:

OTHER SOURCE(S): CASREACT 119:48724

ΙT 148531-01-5P

RN

RL: SPN (Synthetic preparation); PREP (Preparation)

(preparation of) 148531-01-5 CAPLUS

Benzeneethanol,  $\alpha$ -phenyl- $\beta$ -[1-(trimethylsilyl)ethenyl]- (CA CN

INDEX NAME)

ANSWER 31 OF 41 CAPLUS COPYRIGHT 2008 ACS on STN T.3

 $\gamma$ -Silyl tertiary alcs. e.g., Me3SiCH2CH2CMe2OH rearrange in protic acid  $BF3 \cdot 2AcOH$  with 1,2-shift of hydride, Ph, or alkyl groups, and loss of the silyl group to give alkenes e.g., H2C:CHCHMe2. The placing of the silyl group thus controls the carbonium ion rearrangement in a preparatively useful way. Methoxycarbonyl groups do not migrate; instead, cyclopropanes are formed, except when the conformation suitable for cyclopropane formation is unattainable. When the alkene product is 2,2-disubstituted, it can be reprotonated under the reaction conditions and does not therefore always survive. This can be avoided by carrying out the reaction using a Lewis acid on the silyl ether. The starting  $\gamma$ -silyl alcs. are prepared by a variety of versatile methods.

ACCESSION NUMBER: 1989:594181 CAPLUS

DOCUMENT NUMBER: 111:194181

ORIGINAL REFERENCE NO.: 111:32267a,32270a

TITLE: Carbonium ion rearrangements controlled by the

presence of a silyl group

AUTHOR(S): Fleming, Ian; Patel, Shailesh K.; Urch, Christopher J.

CORPORATE SOURCE: Univ. Chem. Lab., Cambridge, CB2 1EW, UK

Journal of the Chemical Society, Perkin Transactions SOURCE: 1: Organic and Bio-Organic Chemistry (1972-1999)

(1989), (1), 115-24

CODEN: JCPRB4; ISSN: 0300-922X

DOCUMENT TYPE: Journal LANGUAGE: English

CASREACT 111:194181 OTHER SOURCE(S):

123315-07-1P 123315-38-8P ΙT

RL: SPN (Synthetic preparation); PREP (Preparation)

(preparation and boron trifluoride acetic acid complex mediated

rearrangement of, alkene by)

RN 123315-07-1 CAPLUS

CN Benzeneethanol,  $\alpha$ -methyl- $\alpha$ -phenyl- $\beta$ -

[(trimethylsilyl)methyl]-, (R\*,R\*)- (9CI) (CA INDEX NAME)

Relative stereochemistry.

RN 123315-38-8 CAPLUS

CN Benzeneethanol,  $\alpha$ -methyl- $\alpha$ -phenyl- $\beta$ -

[(trimethylsilyl)methyl]-, (R\*,S\*)- (9CI) (CA INDEX NAME)

Relative stereochemistry.

L3 ANSWER 32 OF 41 CAPLUS COPYRIGHT 2008 ACS on STN GI

e.g., I.

AB Michael addition of Me3SiCH:C(OEt)OSiMe3 to  $\alpha, \beta$ -unsatd. ketones, e.g., RCOCH:CHR1 (R = Me, Et, Ph; R1 = H, Ph), in the presence of TiCl4 and Ti(OCHMe2)4 gave 51-98% keto esters, e.g., RCOCH2CHR1CH(SiMe3)CO2Et (same R, R1). Selective reduction of the keto esters with NaBH4 gave 76-98% hydroxy esters, e.g., HOCHRCH2CHR1CH(SiMe3)CO2Et. Deprotonation and addition of excess R2CHO (R2 = Ph, H) gave, after alkylation, Peterson-type olefination, and lactonization, 40-89%  $\alpha$ -ylidene  $\delta$ -lactones,

ACCESSION NUMBER: 1987:598007 CAPLUS

DOCUMENT NUMBER: 107:198007

ORIGINAL REFERENCE NO.: 107:31759a,31762a

TITLE: Michael-type addition of O-ethyl-C,O-

bis(trimethylsilyl)ketene acetal and its application

to the synthesis of  $\alpha$ -ylidene  $\delta$ -lactones

AUTHOR(S): Matsuda, Isamu

CORPORATE SOURCE: Fac. Eng., Nagoya Univ., Nagoya, 464, Japan

SOURCE: Journal of Organometallic Chemistry (1987), 321(3),

307-16

CODEN: JORCAI; ISSN: 0022-328X

DOCUMENT TYPE: Journal LANGUAGE: English

OTHER SOURCE(S): CASREACT 107:198007

IT 111022-93-6P 111022-94-7P

RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)

(preparation and reduction of, with sodium borohydride)

RN 111022-93-6 CAPLUS

CN Benzenepentanoic acid,  $\delta$ -oxo- $\beta$ -phenyl- $\alpha$ -(trimethylsilyl)-, ethyl ester, (R\*,S\*)- (9CI) (CA INDEX NAME)

Relative stereochemistry.

RN 111022-94-7 CAPLUS

CN Benzenepentanoic acid,  $\delta$ -oxo- $\beta$ -phenyl- $\alpha$ -(trimethylsilyl)-, ethyl ester, (R\*,R\*)- (9CI) (CA INDEX NAME)

Relative stereochemistry.

IT 111023-01-9P 111137-47-4P 111137-48-5P

111137-49-6P

RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)

(preparation, olefination, and lactonization of)

RN 111023-01-9 CAPLUS

CN Benzenepentanoic acid,  $\delta$ -hydroxy- $\beta$ -phenyl- $\alpha$ - (trimethylsilyl)-, ethyl ester, ( $\alpha$ R\*, $\beta$ S\*, $\delta$ S\*)- (9CI) (CF INDEX NAME)

RN 111137-47-4 CAPLUS

CN Benzenepentanoic acid,  $\delta$ -hydroxy- $\beta$ -phenyl- $\alpha$ - (trimethylsilyl)-, ethyl ester, ( $\alpha$ R\*, $\beta$ S\*, $\delta$ R\*)- (9CI) (CA INDEX NAME)

RN 111137-48-5 CAPLUS

CN Benzenepentanoic acid,  $\delta$ -hydroxy- $\beta$ -phenyl- $\alpha$ - (trimethylsilyl)-, ethyl ester, ( $\alpha$ R\*, $\beta$ R\*, $\delta$ S\*)- (9CI) (CA

$$\begin{array}{c|cccc} & \text{Ph} & \text{Ph} & \text{SiMe3} \\ & | & | & | \\ \text{HO-CH-CH}_2\text{-CH-CH-C-OEt} \\ & | & | \\ & & \text{O} \end{array}$$

RN 111137-49-6 CAPLUS

CN Benzenepentanoic acid,  $\delta$ -hydroxy- $\beta$ -phenyl- $\alpha$ - (trimethylsilyl)-, ethyl ester, ( $\alpha$ R\*, $\beta$ R\*, $\delta$ R\*)- (9CI) (CA INDEX NAME)

$$\begin{array}{c|cccc} & \text{Ph} & \text{Ph} & \text{SiMe3} \\ & | & | & | \\ \text{HO-CH-CH}_2\text{-CH-CH-C-OEt} \\ & | & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & & | \\ & | \\ & & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ & | \\ &$$

L3 ANSWER 33 OF 41 CAPLUS COPYRIGHT 2008 ACS on STN

AB RCH:CLiSnMe3 (I; R = Me, Bu, cyclohexyl, Me3C, Ph), prepared from RCH:C(SnMe3)2 and MeLi, reacted with electrophiles MeOD, Me2SO4, and Me3SiCl to give RCH:CDSnMe3, RCH:CMeSnMe3, and RCH:C(SiMe3)(SnMe3) (II), resp. Lithiation of II (same R) gave RCH:CLiSiMe3 (III), which were methylated to give RCH:CMeSiMe3. Treating III (R = Me, Bu, cyclohexyl) with MeOD led to reformation of II whereas III (R = Ph) and MeOD gave (E)-PhCH:CDSiMe3. (E)-I (R = Ph, CMe3) and (E)-II (R = Ph) reacted with R1CHO (R1 = H, Me, Et, CHMe2, Ph, PhCH:CH, MeCH:CH) and R2COPh (R2 = Ph, C6H4Me-2) with 1,2-addition to give 62-87% (E)-RCH:C(MMe3)CHR1OH or 53-91% (E)-RCH:C(MMe3)CPhR2OH (M = Si, Sn); PhCH:CHCOR3 (R3 = Ph, CMe3) and (E)-I (R = Ph, CMe3) or (E)-II (R = Ph) reacted with 1,4-addition to form 72-86% (E)-RCH:C(MMe3)CHPhCH2COR3 (M = Si, Sn).

ACCESSION NUMBER: 1985:471365 CAPLUS

DOCUMENT NUMBER: 103:71365

ORIGINAL REFERENCE NO.: 103:11493a,11496a

TITLE: Formation of  $\alpha$ -silylvinyllithium reagents:

reactions of  $\alpha$ -silyl- and  $\alpha$ -

stannylvinyllithiums with aldehydes and ketones

AUTHOR(S): Mitchell, Terence N.; Reimann, Werner

CORPORATE SOURCE: Abt. Chem., Univ. Dortmund, Dortmund, 4600/50, Fed.

Rep. Ger.

SOURCE: Journal of Organometallic Chemistry (1985), 281(2-3),

163-71

CODEN: JORCAI; ISSN: 0022-328X

DOCUMENT TYPE: Journal LANGUAGE: English

OTHER SOURCE(S): CASREACT 103:71365

IT 97558-18-4P

RL: SPN (Synthetic preparation); PREP (Preparation)

(preparation of)

RN 97558-18-4 CAPLUS
CN 4-Penten-1-one, 1,3,5-triphenyl-4-(trimethylsilyl)-, (F

N 4-Penten-1-one, 1,3,5-triphenyl-4-(trimethylsilyl)-, (E)- (9CI) (CA INDEX NAME)

Double bond geometry as shown.

L3 ANSWER 34 OF 41 CAPLUS COPYRIGHT 2008 ACS on STN

AB Alkyl and aryl tertiary alcs. with a  $\gamma$ -silyl group generally undergo a carbonium ion rearrangement in acid to give an alkene with the loss of the silyl group. E.g., Me3Si(CH2)2C(OH)Me2 in BF3/AcOH/CH2Cl2 at 0° for 15 min gave CH2:CHCHMe2 quant. The scope of this reaction was investigated and it was shown that hydride and Ph shifts are facile; that hydride migrates faster than an alkyl group when it is Me, or when the migration terminus has 2 aryl groups; and that larger alkyl groups migrate faster than hydride, except where there are ring residues.

ACCESSION NUMBER: 1981:549839 CAPLUS

DOCUMENT NUMBER: 95:149839

ORIGINAL REFERENCE NO.: 95:25067a,25070a

TITLE: Carbonium ion rearrangements controlled by the

presence of a silyl group

AUTHOR(S): Fleming, Ian; Patel, Shailesh K.

CORPORATE SOURCE: Chem. Lab., Univ. Cambridge, Cambridge, CB2 1EW, UK

SOURCE: Tetrahedron Letters (1981), 22(24), 2321-4

CODEN: TELEAY; ISSN: 0040-4039

DOCUMENT TYPE: Journal LANGUAGE: English

OTHER SOURCE(S): CASREACT 95:149839

IT 79238-95-2

RL: RCT (Reactant); RACT (Reactant or reagent)

(elimination/rearrangement reactions of, acid-catalyzed)

RN 79238-95-2 CAPLUS

CN Benzeneethanol,  $\alpha$ -methyl- $\alpha$ -phenyl- $\beta$ -

[(trimethylsilyl)methyl]- (CA INDEX NAME)

$$\begin{array}{c|c} \text{Ph} & \\ | & \\ \text{Me-C-----} \text{CH---} \text{CH}_2\text{----} \text{SiMe}_3 \\ | & | & \\ \text{OH Ph} \end{array}$$

L3 ANSWER 35 OF 41 CAPLUS COPYRIGHT 2008 ACS on STN

AB Me3Si radicals formed by the photodecompn. of (Me3Si)2Hg (I) [4656-04-6] were responsible for the radical photopolymn. of styrene (II) [100-42-5] in presence of I. The polymerization rate was expressed by the equation Rp = K[I]1/2[II]. IR and NMR of the polymer showed that Me3Si groups were incorporated. Reaction of equimolar amts. of I and II in benzene under UV irradiation gave 22% of the radical coupling product 2,2,7,7-tetramethyl-4,5-diphenyl-2,7-disilaoctane [41115-16-6]. N-trimethylsiloxy-2,4,6-tri-tert-butylanilino radical [62489-01-4] was obtained by a spin trapping technique using 2,4,6-tri-tert-butylnitrosobenzene as the trapping agent.

ACCESSION NUMBER: 1977:156039 CAPLUS

DOCUMENT NUMBER: 86:156039

ORIGINAL REFERENCE NO.: 86:24523a,24526a

TITLE: Radical polymerization by silyl radicals.

Photopolymerization of styrene by

bis(trimethylsilyl)mercury

AUTHOR(S): Ikeda, Hisayoshi; Miura, Yozo; Kinoshita, Masayoshi

CORPORATE SOURCE: Fac. Eng., Osaka City Univ., Osaka, Japan SOURCE: Makromolekulare Chemie (1976), 177(9), 2647-55

CODEN: MACEAK; ISSN: 0025-116X

DOCUMENT TYPE: Journal

LANGUAGE: English

IT 41115-16-6

RL: USES (Uses)

(coupling product, of radical reaction of styrene with

bis(trimethylsilyl)mercury)

RN 41115-16-6 CAPLUS

CN Silane, (2,3-diphenyl-1,4-butanediyl)bis[trimethyl- (9CI) (CA INDEX NAME)

L3 ANSWER 36 OF 41 CAPLUS COPYRIGHT 2008 ACS on STN

AB Several Pt(II) complexes containing chiral phosphines, (R)—benzylmethylphenylphosphine (BMPP), (R)—methylphenylpropylphosphine (MPPP), and methyldiphenylphosphine were prepared Catalytic asymmetric hydrosilylation was achieved for the 1st time in the reaction of MeCl2SiH with 1,1-disubstituted prochiral olefins,  $\alpha$ -methylstyrene, 2,3-dimethyl-1-butene, and 2-methyl-1-butene, using a Pt catalyst precursor [LPtCl2]2 L = BMPP, MPPP), and partly optically active adducts RMeCHCH2SiMeCl2 (R = Ph, Me2CH) were obtained. With Cl3SiH, the asymmetric addition reaction was always accompanied by isomerization or dimerization of the olefins. The chiral Pt complex-catalyzed addition-cyclization of 4-pentenyldimethylsilane also gave rise to an optically active 2-methyl-1-silacyclopentane derivative

ACCESSION NUMBER: 1977:5526 CAPLUS

DOCUMENT NUMBER: 86:5526
ORIGINAL REFERENCE NO.: 86:959a,962a

TITLE: Catalytic asymmetric hydrosilylation of olefins. I.

Chiral phosphine-platinum(II) complexes as

hydrosilylation catalysts

AUTHOR(S): Yamamoto, Keiji; Hayashi, Tamio; Zembayashi, Michio;

Kumada, Makoto

CORPORATE SOURCE: Dep. Synth. Chem., Kyoto Univ., Kyoto, Japan

SOURCE: Journal of Organometallic Chemistry (1976), 118(2),

161-81

CODEN: JORCAI; ISSN: 0022-328X

DOCUMENT TYPE: Journal LANGUAGE: English IT 61283-78-1P 61283-79-2P

RL: SPN (Synthetic preparation); PREP (Preparation)

(preparation of) 61283-78-1 CAPLUS

CN Silane, trichloro(4-methyl-2,4-diphenylpentyl)- (9CI) (CA INDEX NAME)

RN

L3 ANSWER 37 OF 41 CAPLUS COPYRIGHT 2008 ACS on STN

AB Lithiation of vinylic metalloids gives anion-radicals which, if quenched quickly, give synthetically-useful bimol. coupling. Thus, treating Ph2Si(CH:CH2)2 with 2 equivalent Li in Me3COH-THF gave 50% 1,1-diphenylsilacyclopentane and 50% Et2SiPh2. Ph3M(CH:CH2)(M = Si, Ge) gave either  $\alpha-$  or  $\beta-$ coupling according to the stabilization of the intermediate radical anion. Ph3Sn(CH:CH2) gave only Ph3SnSnPh3 when treated with K mirror at  $-78^{\circ}$ . Polymerization is suppressed.

ACCESSION NUMBER: 1973:159767 CAPLUS

DOCUMENT NUMBER: 78:159767

ORIGINAL REFERENCE NO.: 78:25659a,25662a

TITLE: Chemistry of alkali metal-unsaturated hydrocarbon

adducts. IX. Radical-anionic coupling of Group IV

organometalloidal compounds

AUTHOR(S): Eisch, John J.; Gupta, Goutam

CORPORATE SOURCE: Dep. Chem., State Univ. New York, Binghamton, NY, USA

SOURCE: Journal of Organometallic Chemistry (1973), 50(1),

C23-C25

CODEN: JORCAI; ISSN: 0022-328X

DOCUMENT TYPE: Journal LANGUAGE: English

IT 41115-16-6P

RN

RL: SPN (Synthetic preparation); PREP (Preparation)

(preparation of) 41115-16-6 CAPLUS

CN Silane, (2,3-diphenyl-1,4-butanediyl)bis[trimethyl- (9CI) (CA INDEX NAME)

L3 ANSWER 38 OF 41 CAPLUS COPYRIGHT 2008 ACS on STN

AB A sealed tube with Et3GeLi from 11.38 g. (Et3Ge)2Hg and 1 g. Li, in C6H6, in the presence of 300 ml. condensed C2H4 (addition of the olefin repeated twice), kept overnight gave 67.8% Et4Ge. Reaction of Et3SiLi and CH2:CH2 gave 43% Et4Si; with MeCH:CH2 the yield of Et3PrSi was 36%. Et3SiLi in C6H6 heated with 1-hexene 8 hrs. at 50° gave 16.3% C6H13SiEt3, b200 171-6°; similar reaction at 90° 21 hrs. gave 8.6% C6H13GeEt3, b20 117°, n20D 1.4580. Et3GeLi and C2H4 kept 3 days at room temperature, and Et3GeBr (free of 0) added, reacted with heat evolution to

give rapidly 91% LiBr and 69.4% (Et3GeCH2)2, b1 110-12°, 1.4780.

PhCH:-CH2 and Et3SiLi in C6H6 reacted at room temperature to give in 1 day 23.5%

PhCH2CH2SiEt3, b1  $105-7^{\circ}$ , and 36.2% 1-triethylsilyl-2,4-diphenylbutane, b1  $160-2^{\circ}$ . Similarly, Et3GeLi gave Et3GeCH2CH2Ph, b1.5  $107^{\circ}$ , 1.5078. Stilbene and Et3GeLi in C6H6 gave 50% (Et3GeCHPh)2, b1.5  $148-9^{\circ}$ , 1.5550. PhC.tplbond.CPh and Et3GeLi

gave Et3GeCPh:CHPh, b1 140°, 1.5750. An equimolar mixture of stilbene and Et3GeLi treated with Et3GeBr gave 29.4% (Et3GeCPhH)2, m. 81-2°. Similarly was prepared Et3GeCPh:CHGeEt3, b1 91-3°, 1.5120, and Et3GeCPh:-CPhGeEt3, m. 64°. Et3GeLi in C6H6 and Ph2CO in 2 days at room temperature followed by an aqueous treatment gave 44.2%

Et3GeCPh2OH, b1 143-5°, 1.5770.

ACCESSION NUMBER: 1969:29022 CAPLUS

DOCUMENT NUMBER: 70:29022
ORIGINAL REFERENCE NO.: 70:5437a,5440a

TITLE: Addition of triethylsilyl- and triethylgermyllithium

to unsaturated bonds

AUTHOR(S): Vyazankin, N. S.; Gladyshev, E. N.; Arkhangel'skaya,

E. A.; Razuvaev, G. A.; Korneva, S. P.

CORPORATE SOURCE: Lab. Stabil. Polim., Gorki, USSR

SOURCE: Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya

(1968), (9), 2081-5

CODEN: IASKA6; ISSN: 0002-3353

DOCUMENT TYPE: Journal LANGUAGE: Russian

IT 21184-10-1P

RN

RL: SPN (Synthetic preparation); PREP (Preparation)

(preparation of) 21184-10-1 CAPLUS

CN Silane, (2,4-diphenylbutyl)triethyl- (8CI) (CA INDEX NAME)

L3 ANSWER 39 OF 41 CAPLUS COPYRIGHT 2008 ACS on STN

AB The addition of Ph3SiLi (I) to trans-stilbene (II) yielded a variety of products, from which [Ph3Si(Ph)CH]2 (III) and Ph3Si(Ph)CHCHPhCHPhCH2Ph (IV) have been isolated and identified. In connection with the structure proof of these compds. the identity of (PhCH2CHPh)2 (V), m. 89-91°, has been confirmed by several varied syntheses. I from 25.2 g. (Ph2Si)2 and 0.4 g. Li in 100 cc. (CH2OMe)2 treated with 18.0 g. II in 150 cc. C6H6, the excess Li removed, the mixture stirred 24 hrs. at room temperature, hydrolyzed with H2O, and the white solid precipitate (10 g.) recrystd. twice

from

C6H6 yielded 9.0 g. III, m. 250-2°; the aqueous layer of the filtrate extracted 3 times with 100-cc. portions C6H6, the combined non-aqueous solns. dried and evaporated in vacuo, the residual oily solid recrystd. from ligroine (b. 75-115°), and the crude product again recrystd. yielded 7.4 g. IV, white crystals, m.  $155-7^{\circ}$ ; the mother liquors evaporated to dryness gave a viscous pale yellow sirup which could be distilled in part at  $130-70^{\circ}$  and 0.7mm. I (0.026 mole) treated with 0.013 mole II, and the mixture stirred 0.5 hr. and then hydrolyzed gave only 2% III, m.  $250-2^{\circ}$ , and 16% IV, m.  $154-7^{\circ}$ , together with much polymeric material. A similar reaction in a min. of (CH2OMe)2 diluted with 8 vols. Et20 gave no III and only 15% IV. I (0.011 mole) in 13 cc. (CH20Me)  $^2$ treated with 1.0 g. tolan in 15 cc. C6H6, and the dark red-black mixture stirred 0.5 hr. and hydrolyzed gave 0.31 g. III, m. 250-2°. III (2.0 g.), 55 cc. dioxane, 25 cc. Methyl Cellosolve, 2.0 g. KOH, and 3 cc. H2O refluxed 5.5 hrs., the solution evaporated to dryness in vacuo, the residue neutralized with dilute HCl and dissolved in Et2O, the solution dried and evaporated to dryness in vacuo, and the residue recrystd. from ligroine (b.  $60-70^{\circ}$ ) yielded 1.25 g. Ph3SiOH, m. 149-51°; the mother

liquor evaporated to dryness and the residue recrystd. from aqueous  ${\tt EtOH}$  yielded

0.35 g. (PhCH2)2, m. 51-2°. Ph3SiCHBrPh (VI) (5.0 g.) in 35 cc. C6H6 refluxed with 0.5 g. Na, the mixture treated with 35 cc. xylene, the C6H6 distilled off to 115° distillation temperature, the residual dark brown solution refluxed 12 hrs., hydrolyzed cautiously with H2O, neutralized with acid, and filtered, and the filter residue (0.75 g.) recrystd. from PhMe-ligroine (b. 90-100) gave III, m. 249-52°; the xylene layer of the filtrate gave an addnl. 0.34 g. III, and 0.34 g. compound, m. 235-8°, presumably a 2nd isomer of III, and 2.0 g. unchanged VI. Tetraphenylthiophene (5.0 g.) reduced with Na and AmOH by the method of Bergmann (C.A. 30, 4857.9) yielded 1.65 g. 1,2-diphenyl-3-benzylhydrindene (VII), m.  $181-2^{\circ}$ , and 1.04 g. V, white needles, m.  $89-91^{\circ}$ (from MeOH). (PhCH:CPh)2 (VIII), m. 183-4°, (0.7 g.) in 25 cc. refluxing AmOH treated during 2 hrs. with 2.0 g. Na, the mixture poured into excess 50% AcOH, and the precipitate (0.35 g.) recrystd. from 2:1 EtOH-CHCl3 yielded 0.23 g. VII, m. 180-2°; the filtrate steam distilled, and the gummy distillation residue recrystd. from MeOH yielded 0.25 g. V, white needles, m. 88-90°. VIII (3.0 g.) in 30 cc. Et20, 10 cc. (CH2OMe)2, and 20 cc. C6H6 stirred 3 hrs. with  $0.5~\mathrm{g}$ . Li and the dark brown solution poured rapidly into EtOH yielded 0.93 g. VII, m. 180-2°; the filtrate worked up gave 0.90 g. V, m. 89-91°. VIII (0.35 g.) in 35 cc. pure dioxane hydrogenated 22 hrs. at 1300 lb. pressure over Raney Ni gave 0.17 g. unchanged VIII, m.  $183-4^{\circ}$ , and 0.21 g. white needles which recrystd. from MeOH yielded 0.17 g. V, m. 89-90°. ACCESSION NUMBER: 1956:44510 CAPLUS DOCUMENT NUMBER: 50:44510 ORIGINAL REFERENCE NO.: 50:8591c-i TITLE: The reactions of triphenylsilyllithium with stilbene Brook, A. G.; Tai, K. M.; Gilman, Henry AUTHOR(S): CORPORATE SOURCE: Iowa State Coll., Ames SOURCE: Journal of the American Chemical Society (1955), 77, 6219-21 CODEN: JACSAT; ISSN: 0002-7863 DOCUMENT TYPE: Journal LANGUAGE: Unavailable 18822-25-8P, Silane, triphenyl(1,2,3,4-tetraphenylbutyl)-ΙT RL: PREP (Preparation) (preparation of) RN 18822-25-8 CAPLUS CN Silane, triphenyl(1,2,3,4-tetraphenylbutyl)- (8CI) (CA INDEX NAME)

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cf. C.A. 49, 10977d. Electrophilic substitution in the 5-OH (I), 5-AcNH
(II), and 5-NH2 (III) derivs. of benzothiophene (IV) was found to occur at the 4-position. This is analogous to the behavior of similarly substituted naphthalene derivs. Unlike 2-C10H7OH, I undergoes reactions at both positions ortho to the OH group under nearly the same conditions. When the S atom in IV is oxidized to the sulfone stage, orientation in the benzene ring is changed from predominant 4-substitution to predominant 6-substitution. The results are rationalized in terms of the current theory. 2,5-C1(O2N)C6H3CHO (V) (66 g.), 57 g. HC(OEt)3, 0.75 g. NH4Cl, and 63 cc. dry EtOH refluxed 0.5 h. yielded 82 g. Et acetal of V, b2-3 142-5°, and a middle fraction, b2 142-3°, nD20 1.5312, d31 1.2344. V in EtOH added with stirring to 1 equivalent Na2S solution, and the

mixture treated with C1CH2CO2Na or C1CH2CO2Et yielded 22-38% 5-nitro-2-benzothiophenecarboxylic acid, which decarboxylated and extracted with Et2O gave 5-nitrobenzothiophene (VI). VI (5.0 g.) in 100 cc. absolute EtOH hydrogenated 1 h. over 0.5 g. 5% Pd-C gave III. I (4.1 g.) in 35 cc. C6H6 refluxed 1 h. with 2.8 g. Ac2O, the solvent removed, and the residue (5.1 g.) recrystd. from EtOH yielded the acetate (VII) of I, m. 69°. II (7.3 g.) in 30 cc. AcOH treated with cooling with 2.5 cc. concentrated HNO3, the mixture kept 4 h. at room temperature and poured into excess ice

and H2O, and the crude precipitate (7.8 g.) recrystd. from 50 cc. EtOH gave 6.3 g. 4-NO2 derivative (VIII) of II, m. 131-2°. VIII (0.25 g.) in 3 cc. AcOH heated 1 h. on the steam bath with 1-3 cc. 30% H2O2, the mixture heated 1 h. on the steam bath and diluted with excess H2O, and the precipitate (67%) recrystd. twice from EtOH yielded the 1,1-dioxide of VIII, decomposed at 227°. VIII (3.5 g.) heated 15 min. with an equivalent NaOH in 55 cc. 90% EtOH, the mixture treated with 75 cc. H2O, and the product (2.8 g.) recrystd. from MeOH gave 5-amino-4-nitrobenzothiophene (IX), yellow needles, m. 190°. IX (4.1 g.) in 100 cc. 50% by volume H2SO4 diazotized with 1.5 g. NaNO2 at 0°, the mixture treated with 8 cc. 50% aqueous H3PO2, the solution kept at 0° overnight and then 8 h. at room temperature and extracted with 300 cc. CHCl3, the extract washed with 10% aqueous NaOH and

evaporated, and the residue (2.55 g.) recrystd. from Skellysolve C gave 1.95 g. 4-NO2 derivative (X) of IV, m.  $80-2^{\circ}$ . X prepared by the method of Fries, et al. (C.A. 31, 1402.4), and the product (77%) recrystd. from Skellysolve C m.  $84-5^{\circ}$ . X oxidized in the usual manner yielded 85% 1,1-dioxide, m.  $177-8^{\circ}$  (from EtOH). X (2.0 g.) in 30 cc. EtOH hydrogenated 2 h. over 0.2 g. 5% Pd-C gave 4-aminobenzothiophene (XI). Only X prepared from IX could be hydrogenated. XI (0.3 g.) in 36 cc. H2O and 2 cc. H2SO4 diazotized with an equimolar amount NaNO2, the resulting diazonium salt heated 0.5~h. at  $90^{\circ}$  and cooled, the mixture filtered hot, and then cooled, and the solid deposit (0.15 g.) recrystd. from Skellysolve C gave 0.05 g. product, m.  $75-8^{\circ}$ ; the insol. tars extracted with hot H2O, and the aqueous filtrates with Et2O gave an addnl. 0.06 g. 4-hydroxybenzothiophene (XII); the crude XII recrystd. gave material, m. 78-9°. XII (15 mg.) gave 7 mg. aryloxyacetic acid derivative, m. 149-50° (from H2O). III (2.4 g.) in 10 cc. AcOH treated with 2.7 q. Br in 10% AcOH, the mixture warmed a few min. on the steam bath, diluted with 75 cc. H2O, decolorized with Norit A in 100 cc. boiling dilute HCl and precipitated with Na2CO3 or NH4OH, and the precipitate (2.4 g.) recrystd. once

5-amino-4-bromobenzothiophene (XIII), m.  $69-71^{\circ}$ . 5-Acetamido-4-bromobenzothiophene (XIV) (0.15 g.) refluxed 0.5 h. in 20 cc. concentrated HCl yielded 0.10 g. XIII, m.  $70-1^{\circ}$ . II (0.50 g.) and 0.5 g. NaOAc in 5 cc. AcOH treated with 0.42 g. Br in 4 cc. AcOH, the solution heated 15 min. on the steam bath and diluted with H2O, and the precipitate

gave

(0.58 g.) triturated with concentrated HCl followed by washing with Me2CO and NH4OH gave 0.35 g. XI, m. 139-40°; in the absence of NaOAc, 0.89 g. XIV.HBr, m. 153-6°, was obtained. XIII (0.5 g.) in 20 cc. 50% by volume H2SO4 diazotized at 0° with an equivalent amount NaNO2, the solution treated 24 h. at 0° and an addnl. 24 h. at room temperature with 10 cc. 50% H3PO2, extracted with Et2O, and steam distilled, and the resulting oily (0.10

g.) 4-bromobenzothiophene (XV) oxidized gave 0.06 g. 1,1-dioxide (XVI) of XV, m.  $141-3^{\circ}$  (from aqueous EtOH or C6H6). XI (0.50 g.) in 4 cc. dilute HBr converted through the diazonium salt with CuBr and 0.52 g. NaBr to 0.09 g. XV, and this oxidized gave 0.11 g. XVI, m.  $143-4^{\circ}$ . I (0.50 g.) in 8 cc. AcOH treated with 5 cc. AcOH containing 0.54 g. Br and the resulting product (0.75 g.) recrystd. twice from Skellysolve B gave the 4-Br derivative (XVII) of I, m.  $109-10^{\circ}$ . XIII (0.5 g.) in 10 cc. 50% H2SO4 diazotized, the salt solution heated to boiling and extracted with Et2O,

the extract reextd. with 10% aqueous NaOH, and the product (0.11 g.) recrystd. from Skellysolve B gave XVII, m.  $108-9^{\circ}$ . I (0.45 g.) and 0.9 g. NaOAc in 5 cc. AcOH treated at  $10^{\circ}$  with 0.96 g. Br, the product dissolved in Et2O, the solution extracted with 10% aqueous NaOH, the extract treated

with Norit A, and the purified product  $(0.48~\rm g.)$  recrystd. several times from EtOH and H2O gave 3,4-di-Br derivative of I, m. 93-4°. VII  $(0.50~\rm g.)$  in 3 cc. AcOH treated with 0.46 g. Br in 5 cc. AcOH, the mixture warmed 0.5 h. on the steam bath and diluted with H2O, the precipitate extracted from Et2O with

10% aqueous NaOH, and the neutral residue recrystd. gave the acetate (XVIII) of 3-bromo-5-hydroxybenzothiophene (XIX), white needles, m. 100.5-1.0°; the phenolic compound recrystd. from Skellysolve B and from EtOH and H2O gave XIX, m. 137.5-8.0°. XVIII hydrolyzed with dilute aqueous NaOH yielded 89% XIX, fine white powder, m.  $136-7^{\circ}$  with previous melting at 132°, and solidifying to needles at  $134^{\circ}$ . In the presence of 0.5 g. NaOAc in the AcOH the yield of 5-acetamido-3-bromobenzothiophene was 82%; this product was contaminated with a bright red impurity which was not removed by crystallization but was destroyed during the saponification of the compound XIX,  $m. 134-6^{\circ}$ , was also prepared in 25% yield by diazotizing 0.08 g. 5-amino-3-bromobenzothiophene in 15 cc. 50% H2SO4 at 0° and boiling the solution  $\,$  Br (0.093 g.) in 1  $\,$ cc. AcOH added to 0.134 g. XIX in 3 cc. AcOH, and the resulting crude product recrystd. from Skellysolve B gave 0.05 g. 3,4-di-Br derivative of I, m.  $146-8^{\circ}$ . Na (0.36 g.) in 50 cc. EtOH and 2.3 g. I and 4 cc. allyl bromide refluxed 15 min., the mixture diluted with Et20, and extracted

10% aqueous NaOH, and the Et2O solution evaporated gave 2.7 g. 5-allyloxy-benzothiophene (XX). XX (2.7 g.) refluxed 1 h. in 15 cc. PhNMe2, the mixture dissolved in 50 cc. C6H6, the solution extracted with dilute HCl, and

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rearranged product extracted with three 25-cc. portions Claisen alkali, and purified by steam distillation gave 1.80 g. 4-allyl-5-hydroxybenzothiophene (XXII), b15 183-5°;  $\alpha$ -naphthylurethane, m. 166-8°. 4-Allyl-5-allyloxybenzothiophene (XIII) (1.85 g.) refluxed 9.5 h. in 20 cc. PhNMe2 gave 0.95 g. XXIII and 0.60 g. 4,6-diallyl-5hydroxybenzothiophene (XXIV) b2 155-60°; a similar run with 4 h. heating gave 63% XXIII and 23% XXIV, m. 152-4° (from Skellysolve C). The 5-hydroxybenzothiophene derivs. gave with p-diazobenzenesulfonate the following colors: I, red; XVII, red-brown; XXI, red; XXIV, very pale yellow (no reaction). 5-Nitrobenzothiophene oxidized to the 1,1-dioxide, reduced to the amine, a drop of H2SO4 added to a slurry of 5.0 g. amine in 10 cc. Ac20, the mixture filtered, and the cake washed with H2O and recrystd. from EtOH gave 5.2 g. 1,1-dioxide (XXV) of III, m. 225-6°. II (7.9 g.) in 80 cc. AcOH treated 24 h. at room temperature with 40 cc. 30% H2O2 and the mixture diluted with H2O gave 6.7 g. 1,1-dioxide (XXVI) of II, m. 208-13°. XXV (0.18 g.) in 5 cc. EtOH hydrogenated 2 h. at atmospheric pressure over 0.02 g. 5% Pd-C, the solvent evaporated, and

residue recrystd. from EtOH gave 0.18 g. 5-amino-2,3-dihydrobenzothiophene 1,1-dioxide, m. 147-7.5° (from EtOH). XXV (0.90 g.) in 20 cc. H2SO4 (50%) diazotized at 0° with an equimolar amount of NaNO2, the mixture refluxed 15 min. and filtered hot through celite, the filtrate extracted

with Et2O, the Et2O extract reextd. with 10% aqueous NaOH, and the alkaline extract  $\,$ 

acidified gave 0.31 g. 1,1-dioxide of I, m.  $152-2.5^{\circ}$  (from H2O with Norit). Fuming HNO3 (d. 1.50) (10 cc.) treated slowly with stirring at 0° with 4.0 g. XXVI, the mixture held 0.5 h. at 10°, and poured into 500 cc. cold H2O, and the precipitate (4.2 g.) recrystd. from 600

EtOH gave 3.3 g. 6-NO2 derivative (XXVII) of XXVI, m. 215-16°. XXVII

mixture filtered, and the yellow filter residue (2.8 g.) recrystd. from large amts. of Me2CO gave the 6-NO2 derivative (XXVIII) of XXV, fine yellow needles, which gradually decomposed above 270° turning to a blackened mass at 186-90°. XXVIII (0.50 g.) added at -12° to 0.25 g. NaNO2 in 20 cc. concentrated H2SO4, the mixture diluted slowly with ice at  $-10^{\circ}$  to 100cc., treated with 25 cc. cold H3PO2 and a few small crystals CuSO4, kept 4 h. at 10°, and filtered off, the cake washed with aqueous NaHCO3 and extracted with 25 cc. C6H6, and the C6H6 extract evaporated gave 0.12 g. 6-nitrobenzothiophene 1,1-dioxide, m. 181-2° (from EtOH and C6H6). Br (1.6 g.) in 16 cc. AcOH added with stirring at 65° to 1.81 g. XXV in 35 cc. AcOH containing 1.8 g. NaOAc and the mixture cooled gave 2.3 g. 6-Br derivative (XXIX) of XXV, decomposed at 229-31° (from EtOH and sublimed at 2 mm.). XXIX (1.1 g.) in 20 cc. warm 50%  $\rm H2SO4$  diazotized at  $0^{\circ}$  with 0.5 g. NaNO2, the diazonium salt reduced with 20 cc. 50%aqueous  ${\rm H3PO2}$  and a few crystals of CuSO4 during 3 h. at  $10^{\circ}$ , the yellow precipitate extracted continuously with 50 cc. Et2OH, and the extract conductivity to 15 cc. gave 0.55 g. pure 6-bromobenzothiophene 1,1-dioxide (XXX), m.  $139^{\circ}$ ; further concentrated of the mother liquors gave an addnl. 6.75 g. less pure product. 6-Nitrobenzothiophene 1,1-dioxide (2.1 g.) in 50 cc. EtOH hydrogenated over 0.2 g. 5% Pd-C during 1 h., the mixture concentrated to 30 cc., and the resulting yellow needles (1.4 g.) recrystd. from EtOH gave 6-amino-2,3-dihydrobenzothiophene 1,1-dioxide (XXXI), m. 198-200°. XXX (2.45 g.) in 50 cc. EtOH hydrogenated over 0.2 g. 5% Pd-C, and the crude product (1.5 g.) recrystd. from EtOH gave 1.2 g. 6-bromo-2,3-dihydrobenzothiophene 1,1-dioxide (XXXII), m. 142-4°. XXXI (0.50 g.) in 10 cc. 50% H2SO4 diazotized with 0.20 g. NaNO2, the diazonium salt solution added to 50 cc. boiling suspension of CuBr, the mixture boiled 10 min. and filtered, and the solids extracted with Me2CO gave 0.45 g. XXXII, m.  $142-3^{\circ}$  (from EtOH). ACCESSION NUMBER: 1956:44509 CAPLUS DOCUMENT NUMBER: 50:44509 ORIGINAL REFERENCE NO.: 50:8588i,8589a-i,8590a-i,8591a-c Benzothiophene chemistry. VII. Substitution reactions TITLE: of 5-hydroxy- and 5-aminobenzothiophene derivatives AUTHOR(S): Bordwell, F. G.; Stange, Hugo CORPORATE SOURCE: Northwestern Univ., Evanston, IL SOURCE: Journal of the American Chemical Society (1955), 77, 5939-44 CODEN: JACSAT; ISSN: 0002-7863 DOCUMENT TYPE: Journal Unavailable LANGUAGE: 18822-25-8P, Silane, triphenyl(1,2,3,4-tetraphenylbutyl)-ΤТ RL: PREP (Preparation) (preparation of) RN 18822-25-8 CAPLUS Silane, triphenyl(1,2,3,4-tetraphenylbutyl)- (8CI) (CA INDEX NAME) CN Ph Ph Ph Ph-CH2-CH-CH-CH-SiPh3 L3 ANSWER 41 OF 41 CAPLUS COPYRIGHT 2008 ACS on STN

(3.3 g.) in 60 cc. AcOH and 50 cc. concentrated HCl refluxed 0.5 h., the

AB To 0.5 mole SiHCl3 in a bomb, C2H4 was introduced to a pressure of 500 lb./sq. in. and the mixture kept 8 hrs. at  $270-388^{\circ}$ . When the mixture was cooled to room temperature the pressure had dropped to 225 lb./sq. in. The

following products were isolated and identified: 4 g. boiling below 97°, mainly SiHCl3; 31.5 g. EtSiCl3, b. 98-100°; 19.5 g. BuSiCl3, b. 147-9°; 7.0 g. C6H13SiCl3, b. 190°; and 4.5 g. mixture of C8H17SiCl3 and C10H21SiCl3, b32 150-65°. In other examples given the following compds. were identified: AmSiCl3, b. 163-4°; BuEtSiCl2, b. 169-70°; and PrCH:CHSiCl3, b.  $168-71^{\circ}$ . These materials may be used in new coatings and other

compositions. 1956:40498 CAPLUS ACCESSION NUMBER:

DOCUMENT NUMBER: 50:40498 ORIGINAL REFERENCE NO.: 50:7844c-e

Reaction of silanes with unsaturated aliphatic TITLE:

compounds

INVENTOR(S): MacKenzie, Charles A.; Spialter, Leonard; Schoffman,

Milton

PATENT ASSIGNEE(S): Montclair Research Corp.; Ellis-Foster Co.

DOCUMENT TYPE: Patent Unavailable LANGUAGE:

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17995-62-9P. Silane	. trich	loro(2.4-dir	ohenvlbutvl)-	

ΙT 17995-62-9P, Silane, trichloro(2,4-diphenylbutyl)

RL: PREP (Preparation) (preparation of)

RN 17995-62-9 CAPLUS

CN Silane, trichloro(2,4-diphenylbutyl) - (8CI) (CA INDEX NAME)

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